Electronic Supplementary Information

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S1. General information

All reactions and manipulations were performed under an N_2 atmosphere (< 0.1 ppm O_2, H_2O) using an MBraun Glovebox. All glassware was oven-dried (160 °C) overnight prior to use. Benzene was dried over Na and stored over molecular sieves (3 Å). Acetonitrile, dimethyl sulfoxide and dimethylformamide were distilled from CaH_2 and stored over molecular sieves (3 Å). Benzene was distilled from Na/benzophenone and stored over molecular sieves (3 Å). Acetone was stirred over $CaSO_4$ (3 h) and distilled after dynamically drying over molecular sieves (3 Å). THF and toluene were purified using a MBraun SPS-800 system and stored over molecular sieves (3 Å). C_6D_6 was stored over molecular sieves (3 Å). All other chemicals were purchased from major suppliers; liquids were purified by Kugelrohr distillation and freeze-pump-thaw degassed three times prior to use; white phosphorus (P_4) was purified by sublimation; all other chemicals were used as received.

Caution. P_4 is toxic and highly pyrophoric and should be handled, manipulated and quenched with corresponding caution.

Qualitative NMR spectra were recorded at room temperature on Bruker Avance III HD 400 (400 MHz) spectrometers and were processed using MestReNova v14.0.0. Chemical shifts δ, are reported in parts per million (ppm); ^{1}H and ^{13}C shifts are reported relative to $SiMe_4$ and were calibrated to residual solvent peaks, while ^{31}P shifts were referenced externally to 85% H_3PO_4 (aq.).

NMR samples were prepared in the glovebox using NMR tubes fitted with screw caps. Optimization reactions (see section S3), photocatalytic phenylation reactions of $PhPH_2$, Ph_2PH, Ph_4P_2 and Ph_3P (see section S7), and photocatalytic arylation reactions of $NaPH_2$ (see section S8) were analyzed by $^{31}P\{^{1}H\}$ NMR spectroscopy using only a single scan (DS = 0, D1 = 2 s). The accuracy of this method was confirmed by preparing solutions of (*o*-tol)$_3$P or [Ph_4P]Cl of defined concentrations with each 0.05 mmol Ph_3PO in MeCN/C_6H_6 (1.5 mL, 0.5 mL, respectively), and comparing the measured and expected relative integrals of the corresponding signals (Figure S1).

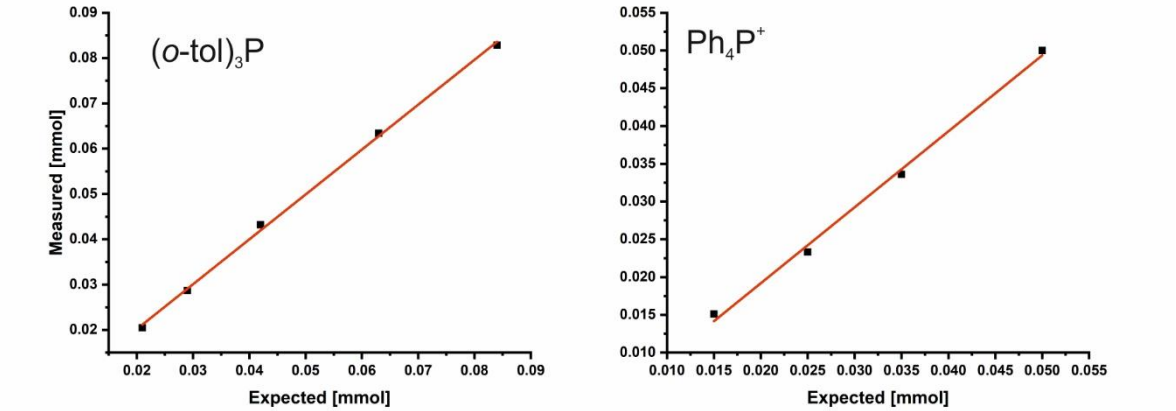


Figure S1. Plots showing the consistency between measured (by integration against 0.05 mmol Ph_3PO using a $^{31}P\{^{1}H\}$ NMR experiment (zgig) with a single scan) and expected (based on mass added) molar quantities of (*o*-tol)$_3$P (left) or [Ph_4P]Cl (right) in MeCN/C_6H_6 (3:1) solutions.

Quantitative measurements for the substrate screening were conducted on Bruker Avance HD III 400 (400 MHz) spectrometers. Yields were determined by 1D $^{31}P\{^{1}H\}$ NMR spectroscopy. In order to meet quantitative conditions, special attention was paid to the following aspects:

- Pulse lengths were calibrated. The O1P of the spectrum was set close to the frequencies of interest to enable maximum excitation.
- T_1 relaxation times were determined for all peaks of interest and a D1 of $\geq 5 \times T_1$ was used to ensure full relaxation between scans.
- The NS was adjusted so that the signal to noise ratio (S/N-ratio) was higher than 100/1. In order to reduce measurement time and to increase the S/N-ratio compared to a standard 1D experiment using only a 90° pulse (zg experiment), the zgig pulse program (inverse gated decoupled) was used, applying proton decoupling during the acquisition time. Since the zgig pulse program uses decoupling, it had to be ensured that any signal enhancement due to nuclear Overhauser effect (NOE) is negligible. Therefore, zg and zgig experiments were conducted and the integrals of the signals of interest were compared. For all reaction mixtures investigated, the integrals corresponding to both the internal standard (Ph_3PO) and the product stayed constant.
- After acquisition, the spectra were processed and integrated, and the yields were determined by referencing the integral of the product to that of the standard Ph_3PO.
- The quantitative NMR spectra of the substrate screening are shown in section S4.

S2. General procedure for photocatalytic functionalization of P_4 (0.04 mmol scale)

To a 10 mL stoppered tube equipped with a stirring bar were added the appropriate aryl bromide or aryl chloride (0.44 mmol, 11.0 equiv. based on the phosphorus atom), NEt_3 (50.2 µL, 0.36 mmol, 9.0 equiv. based on the phosphorus atom), 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (Mes-Acr-BF_4; 2.3 mg, 4.0 µmol, 10 mol% based on the phosphorus atom) and P_4 (1.2 mg, 0.01 mmol, 0.25 equiv., as a stock solution in 65.5 µL benzene). The mixture was dissolved in acetonitrile (0.1 mL). The tube was sealed, placed in a custom-made flask holder (Figure S2, left), and irradiated with nUV light (390 nm, 40 W, Kessil PR160L in a PR160 Rig with Fan Kit, Figure S2, right) for 20 h (for ArBr) or 44 h (for ArCl) (unless stated otherwise). Ph_3PO (0.02 mmol, stock solution in benzene) was subsequently added to act as an internal standard. The resulting mixture was subjected to NMR analysis.

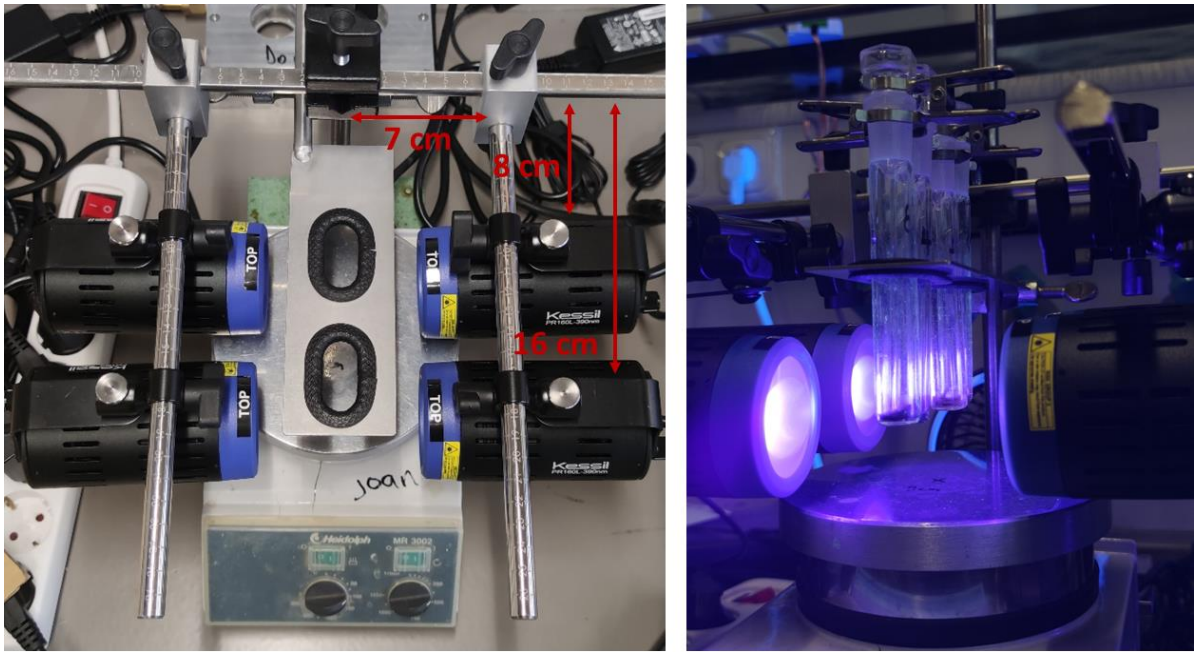
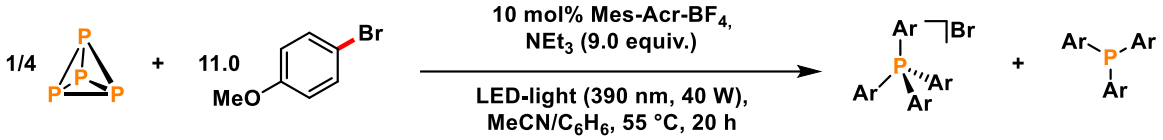


Figure S2. Setup used for photocatalytic reactions at 0.04 mmol scale.

S3. Optimization of reaction conditions

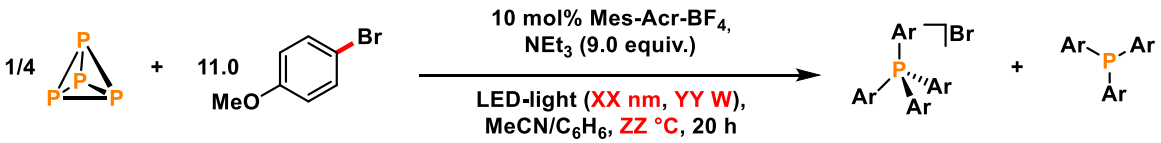
Table S1. Photocatalytic functionalization of P_4 to $[Ar_4P]Br$ and Ar_3P: screening of control experiments.[a]



Entry	Conditions	Full conv. of P_4?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	Standard[a]	✓	47	9
2	No photocatalyst	✗	0	0
3	No light[b]	✗	0	0
4	No NEt_3	✓	0	0
5	No 4-Bromoanisole[c]	✓	0	0
6	4-Fluoroanisole instead of 4-Bromoanisole	✓	0	0
7	4-Iodoanisole instead of 4-Bromoanisole	✓	19	0
8	4-Chloroanisole instead of 4-Bromoanisole	✓	4	14
9	P_{red} instead of P_4[e]	/	0	0

[a] For the general procedure, see section S2. Ar = 4-OMe–C_6H_4–. [b] The reaction flask was heated to 55 °C. [c] No PH_3 formation was observed. [e] The reaction was conducted in MeCN (0.1 mL) and without benzene.

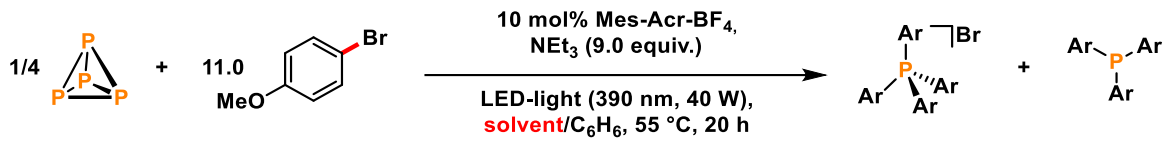
Table S2. Photocatalytic functionalization of P_4 to $[Ar_4P]Br$ and Ar_3P: screening of LEDs at different wavelengths and electrical power.[a]



Entry	LED wavelength[b]	LED power[d]	Full conv. of P_4?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	390 nm	40 W	✓	47	9
2	390 nm	30 W	✓	43	9
3	390 nm	20 W	✓	38	7
4	390 nm	10 W	✓	23	10
5	370 nm	40 W	✓	37	10
6	370 nm[c]	40 W	✓	42	12
7	427 nm	40 W	✓	7	8
8	456 nm	40 W	✓	0	0

[a] For the general procedure, see section S2. Different LEDs were used. Ar = 4-OMe–C_6H_4–. [b] Kessil PR160L LED. [c] PR160L-370 nm Gen 2 LED. [d] The temperature varies with the electrical power. For: 40 W → T = ≈55 °C, 30 W → T = ≈45 °C, 20 W → T = ≈40 °C, 10 W → T = ≈35 °C.

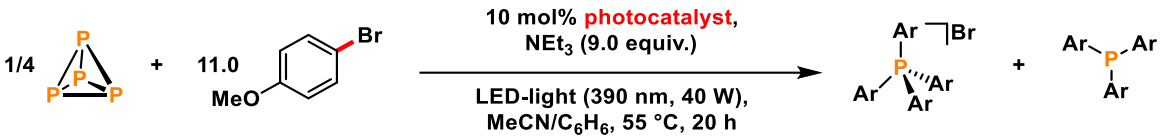
Table S3. Photocatalytic functionalization of P_4 to $[Ar_4P]Br$ and Ar_3P: screening of solvents.[a]

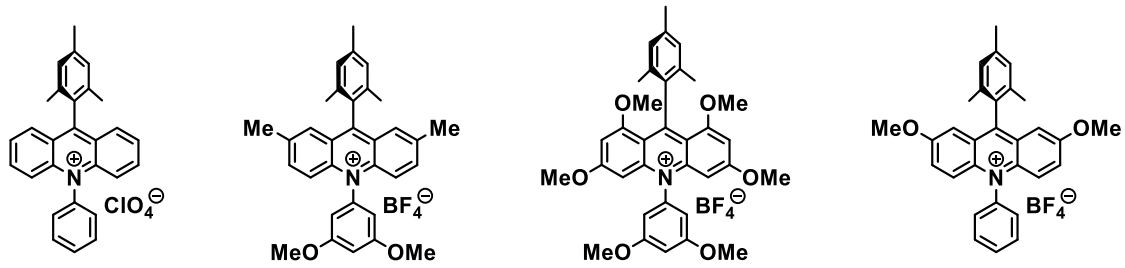


Entry	Solvent	Full conv. of P_4?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	Acetonitrile	✓	47	9
2	DMF	✓	4	6
3	DMSO	✓	16	6
4	Benzene	✓	19	6
5	Acetone	✓	31	5
6	THF	✓	12	8
7	4-Bromoanisole[b]	✓	18	6

[a] For the general procedure, see section S2. Ar = 4-OMe–C_6H_4–. The general procedure (section S2) was modified to use the solvent system indicated (identical solvent volume). [b] Added additionally as solvent (0.1 mL).

Table S4. Photocatalytic functionalization of P_4 to $[Ar_4P]Br$ and Ar_3P: screening of photocatalysts.[a]



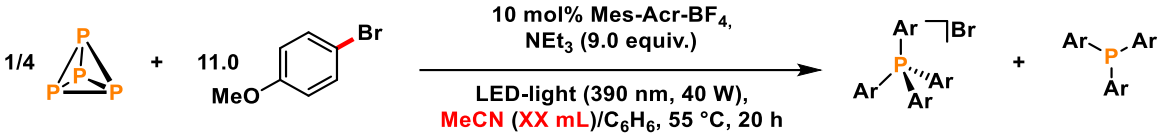


H-Mes-Acr-ClO_4 **Me-Mes-Acr-BF_4** **$(MeO)_2$-Mes-Acr-BF_4** **MeO-Mes-Acr-BF_4**

Entry	Photocatalyst	LED wavelength[b]	Full conv. of P_4?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	H-Mes-Acr-ClO_4	390 nm	✓	9	8
2	Me-Mes-Acr-BF_4	390 nm	✓	34	7
3	$(MeO)_2$-Mes-Acr-BF_4	390 nm	✓	0	5
4	MeO-Mes-Acr-BF_4	390 nm	✓	32	15
5	MeO-Mes-Acr-BF_4	370 nm	✓	27	16
6	MeO-Mes-Acr-BF_4	427 nm	✓	6	9
7	MeO-Mes-Acr-BF_4	456 nm	✓	0	0

[a] For the general procedure, see section S2. Ar = 4-OMe–C_6H_4–. The general procedure (section S2) was modified to use the photocatalyst indicated. [b] All reactions were carried out at 40 W electrical power.

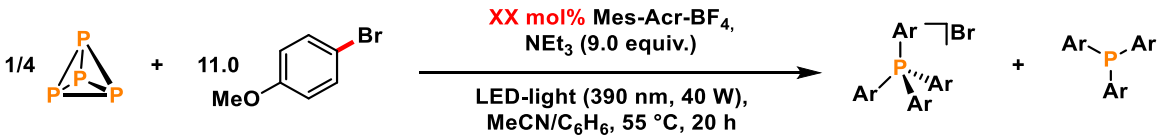
Table S5. Photocatalytic functionalization of P_4 to $[Ar_4P]Br$ and Ar_3P: concentration screening.[a]



Entry	Solvent volume	Full conv. of P_4?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	0.05 mL	✓	47	7
2	0.1 mL	✓	47	9
3	0.25 mL	✓	34	12
4	0.5 mL	✓	30	15
5	1.0 mL	✓	24	17
6	2.0 mL	✓	9	14

[a] For the general procedure, see section S2. Ar = 4-OMe–C_6H_4–. The general procedure (section S2) was modified to use the indicated amount of MeCN.

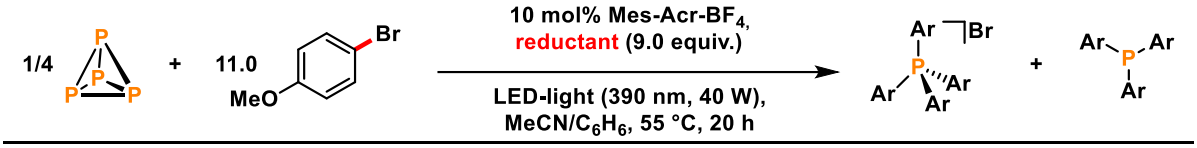
Table S6. Photocatalytic functionalization of P_4 to $[Ar_4P]Br$ and Ar_3P: screening of catalyst loading.[a]



Entry	Catalyst loading	Full conv. of P_4?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	1.0 mol%	✓	7	7
2	5.0 mol%	✓	32	10
3	7.5 mol%	✓	36	13
4	10 mol%	✓	47	9
5	20 mol%	✓	43	8
6	2 x 10 mol%[b]	✓	48	0
7	50 mol%	✓	40	0

[a] For the general procedure, see section S2. Ar = 4-OMe–C_6H_4–. The general procedure (section S2) was modified to use the indicated amount of the photocatalyst Mes-Acr-BF_4. [b] Addition of the second photocatalyst portion (2.3 mg, 10 mol%, 4.0 µmol; in 0.1 mL MeCN) after 20 h irradiation time and then additional 20 h irradiation.

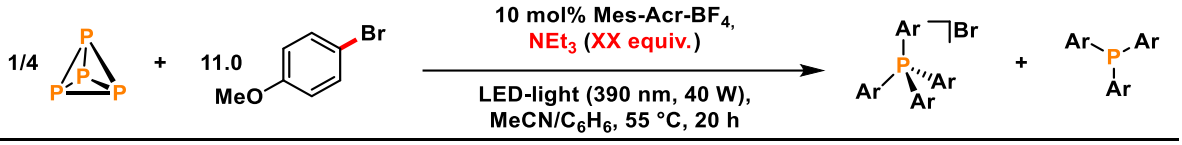
Table S7. Photocatalytic functionalization of P_4 to $[Ar_4P]Br$ and Ar_3P: screening of reductants.[a]



Entry	Reductant	Full conv. of P_4?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	NEt_3	✓	47	9
2	DIPEA	✓	31	9
3	N^nBu_3	✓	29	10
4	Hantzsch ester[b]	✓	0	0
5	DABCO	✓	0	0
6	HN^iPr_2[c]	✓	12	3
7	$NMe_2{}^nPr$	✓	23	12
8	$NaHCO_2$[b]	✓	/	/

[a] For the general procedure, see section S2. Ar = 4-OMe–C_6H_4–. The general procedure (section S2) was modified to use the indicated reducing agent (identical stoichiometry). [b] 0.5 mL MeCN. [c] Additional unidentified signals between 5.0 and 32.0 ppm observed.

Table S8. Photocatalytic functionalization of P_4 to $[Ar_4P]Br$ and Ar_3P: screening of reductant and substrate stoichiometry.[a]

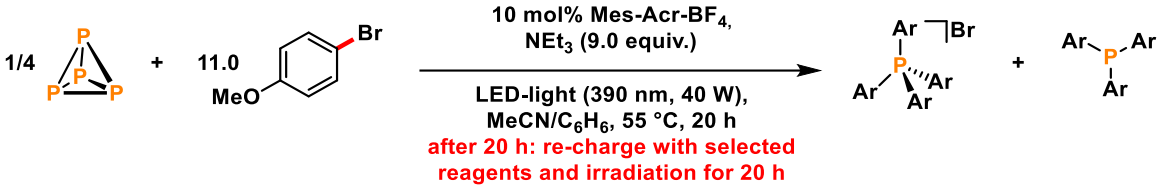


Entry	Stoichiometry[b] NEt_3:4-Bromoanisole	Full conv. of P_4?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	4:44	✓	/	/
2	18:44	✓	26	8
3	24:44	✓	38	9
4	30:44	✓	41	9
5	36:44	✓	45	9
6	42:44	✓	35	9
7	56:44	✓	31	11
8	72:44	✓	25	15
9	36:20	✓	19	12
10	36:32	✓	30	15
11	36:44	✓	47	9
12	36:60	✓	42	7
13	36:80	✓	40	8

[a] For the general procedure, see section S2. Ar = 4-OMe–C_6H_4–. [b] Listed equivalents are defined per P_4 molecule.

Photocatalytic functionalization of P_4 to $[Ar_4P]Br$ and Ar_3P: re-charge experiments.[a]

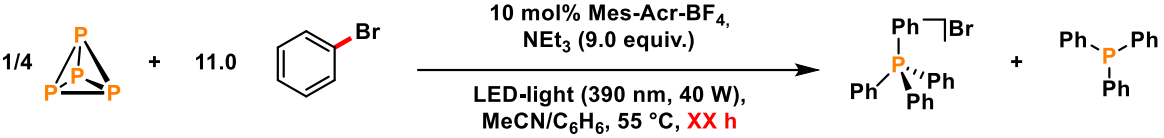
Table S9. Photocatalytic functionalization of P_4 to $[Ar_4P]Br$ and Ar_3P: re-charge experiments.[a]



Entry	Re-charge	Full conv. of P_4?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	No re-charge but irradiation	✓	52	6
2	P_4 + ArBr + NEt_3 + Mes-Acr-BF_4	✓	38	11
3	ArBr + NEt_3 + Mes-Acr-BF_4	✓	58	0
4	ArBr + NEt_3[b]	✓	58	7

[a] For the general procedure, see section S2. Ar = 4-OMe–C_6H_4–. After the reaction was completed following the general procedure, the reaction tube was transferred to a glovebox, re-charged with the indicated reagents and irradiated for an additional 20 h. The reagents were added in equivalent amounts as described in the general procedure; P_4 (1.2 mg, 0.01 mmol, as a stock solution in 65.5 µL benzene); ArBr (55.1 µL, 11.0 equiv., 0.44 mmol); NEt_3 (50.2 µL, 9.0 equiv., 0.36 mmol); Mes-Acr-BF_4 (2.3 mg, 10 mol%, 4.0 µmol; in 0.1 mL MeCN). [b] MeCN (0.1 mL) and benzene (65.5 µL) were added.

Table S10. Photocatalytic functionalization of P_4 to $[Ph_4P]Br$ and Ph_3P: kinetic investigations.[a]



Entry	Time	Full conv. of P_4?	Form. of $[Ph_4P]Br$ / %	Form. of Ph_3P / %	Form.[b] of Ph_2PH / %	Form.[b] of $PhPH_2$ / %	Form.[b] of Ph_4P_2 / %
1	10 min	✗	0	0	✗	✓	✗
2	30 min	✓	0	1	✓	✓	✓
3	1 h	✓	6	9	✓	✓	✓
4	2 h[c]	✓	21	15	✓	✗	✓
5	4 h[c]	✓	38	13	✓	✗	✗
6	6 h[c]	✓	50	8	✗	✗	✗
7	14 h[c]	✓	53	6	✗	✗	✗
8	20 h[c]	✓	63	0	✗	✗	✗
9	44 h	✓	64	0	✗	✗	✗

[a] For the general procedure, see section S2. [b] The formation of Ph_2PH, $PhPH_2$ and Ph_4P_2 was assessed in the $^{31}P\{^1H\}$ NMR spectrum (NS 512). [c] The formation of $[Ph_3P(NEt_2)]Br$ can be observed in the $^{31}P\{^1H\}$ NMR spectrum (NS 512).[1]

S4. Characterization of photocatalytic arylation reactions at 0.04 mmol scale

The conversions were determined by quantitative $^{31}P\{^{1}H\}$ (zgig) NMR experiments (161.98 MHz, 300 K, C_6D_6 capillary) from the reaction solution as described in section S2 (Ph_3PO [0.02 mmol] was used as internal standard, see section S1 for further information).

The $^{31}P\{^{1}H\}$ NMR spectroscopic data for *aryl bromides* is provided after 20 h reaction time, with additional data available for selected substrates after 44 h reaction time (Table S10). The $^{31}P\{^{1}H\}$ NMR spectroscopic data for *aryl chlorides* is provided after 44 h reaction time, with additional data available for selected substrates after 68 h reaction time (Table S10).

The spectroscopic data was assigned to the stated products based on the chemical shifts reported in the literature.[1],[2],[3]

S4.1. $^{31}P\{^{1}H\}$ NMR spectroscopic data for aryl bromides after 20 h and aryl chlorides after 44 h reaction time

Aryl bromides – 20 h reaction time:

S4.1.1 Tetraphenylphosphonium bromide

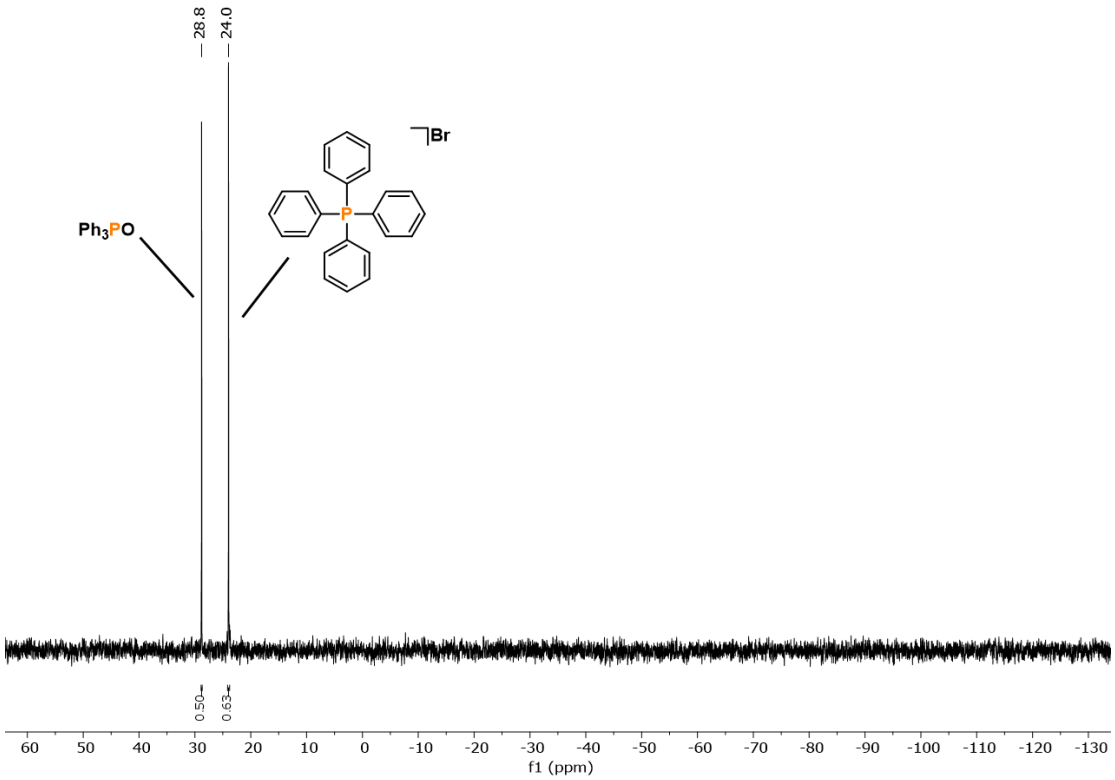


Figure S3. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using bromobenzene.

S4.1.2 Tetrakis(4-methoxyphenyl)phosphonium bromide and tris(4-methoxyphenyl)phosphine

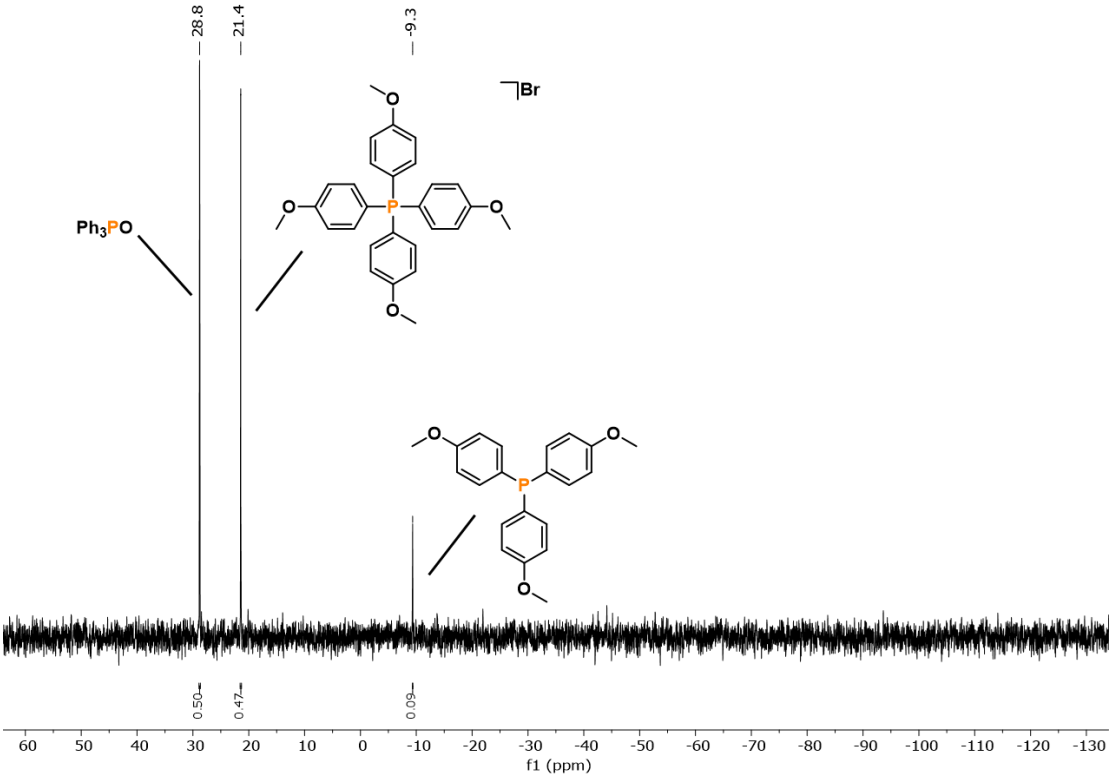


Figure S4. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-bromoanisole.

S4.1.3 Tetrakis(3-methoxyphenyl)phosphonium bromide and tris(3-methoxyphenyl)phosphine

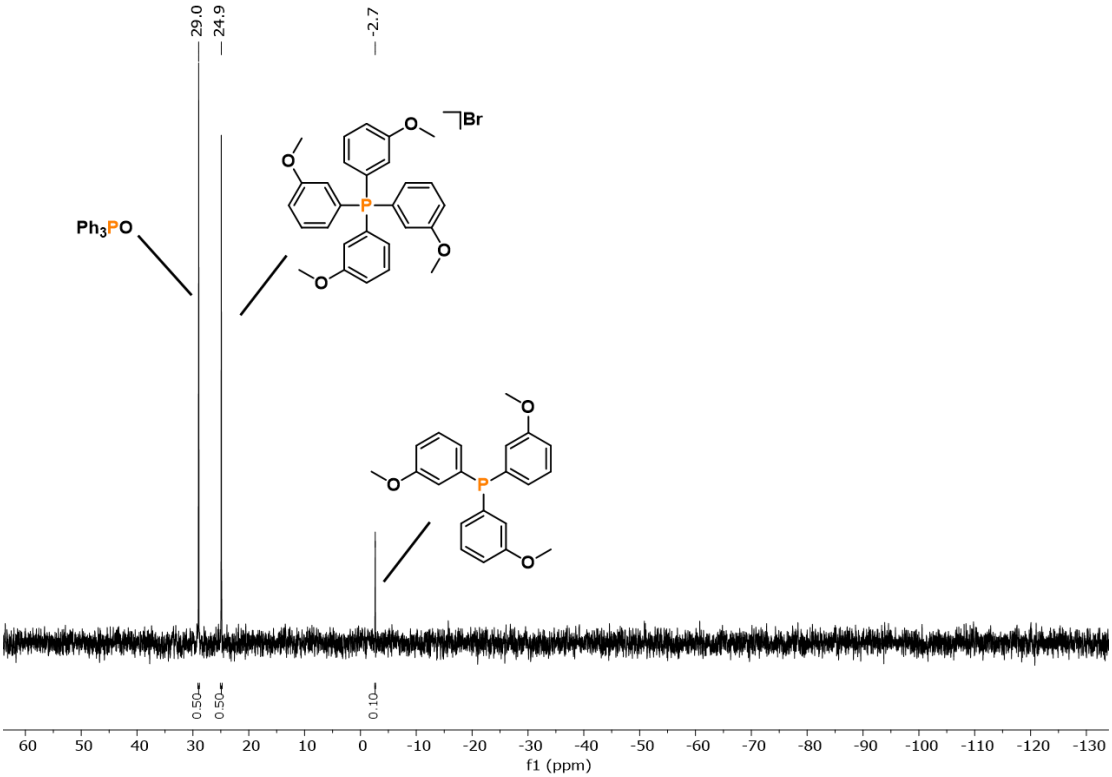


Figure S5. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-bromoanisole.

S4.1.4 Tris(2-methoxyphenyl)phosphine

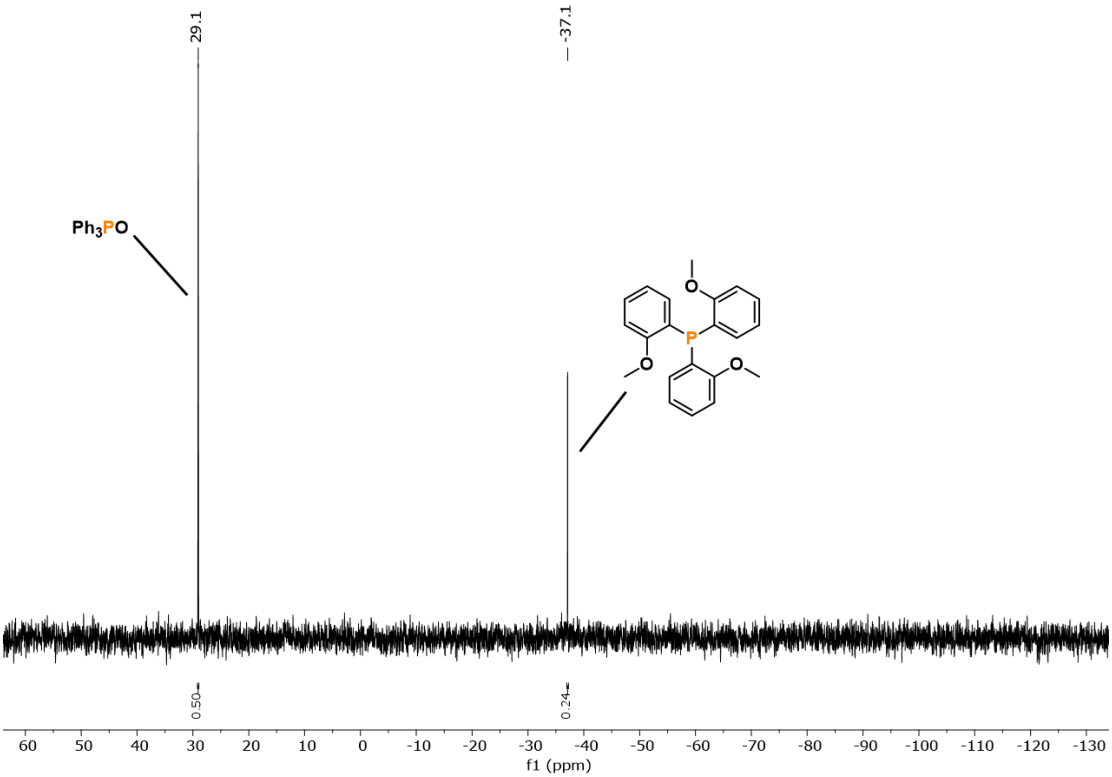


Figure S6. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 2-bromoanisole.

S4.1.5 Tetrakis(3,5-dimethoxyphenyl)phosphonium bromide and tris(3,5-dimethoxyphenyl)-phosphine[4]

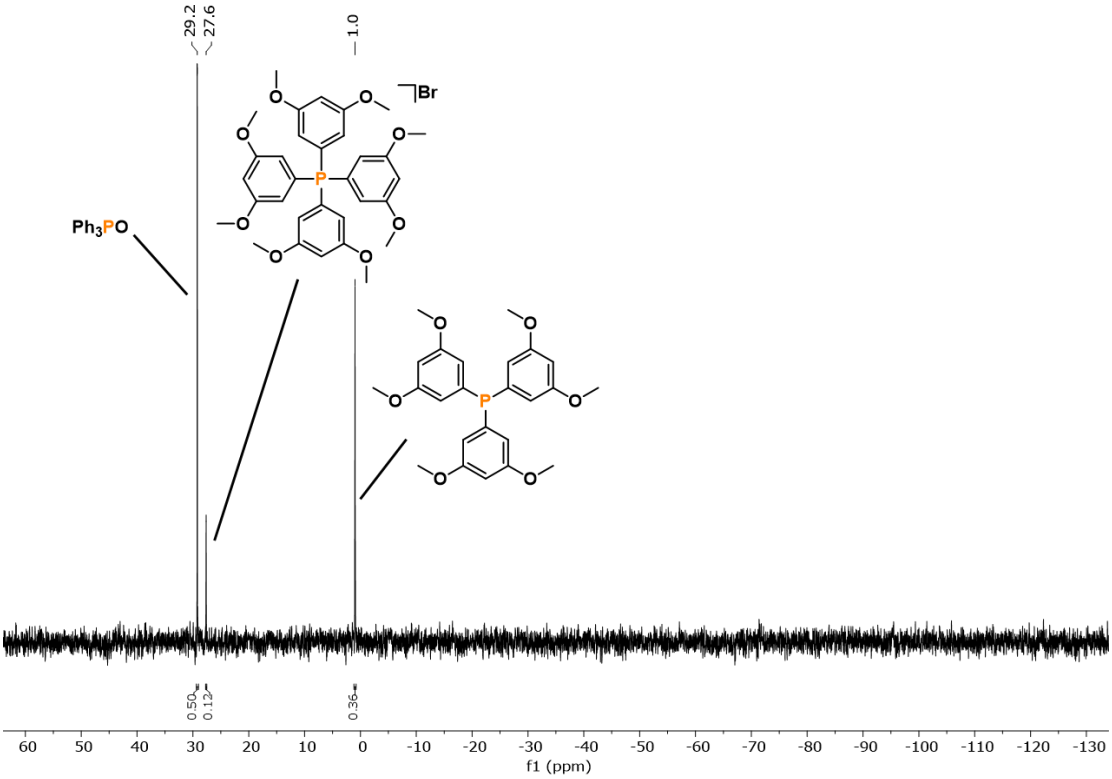


Figure S7. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-bromo-3,5-dimethoxybenzene.

S4.1.6 Tetra(*p*-tolyl)phosphonium bromide and tris(*p*-tolyl)phosphine

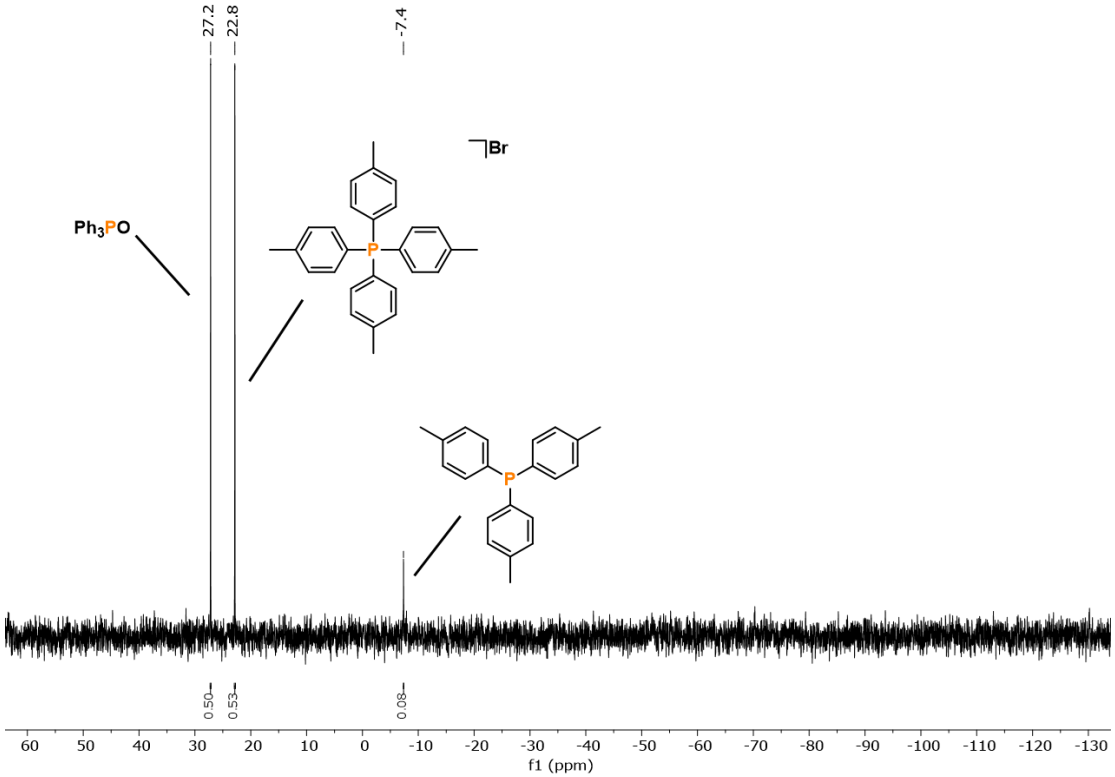


Figure S8. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-bromotoluene.

S4.1.7 Tetra(*m*-tolyl)phosphonium bromide and tris(*m*-tolyl)phosphine

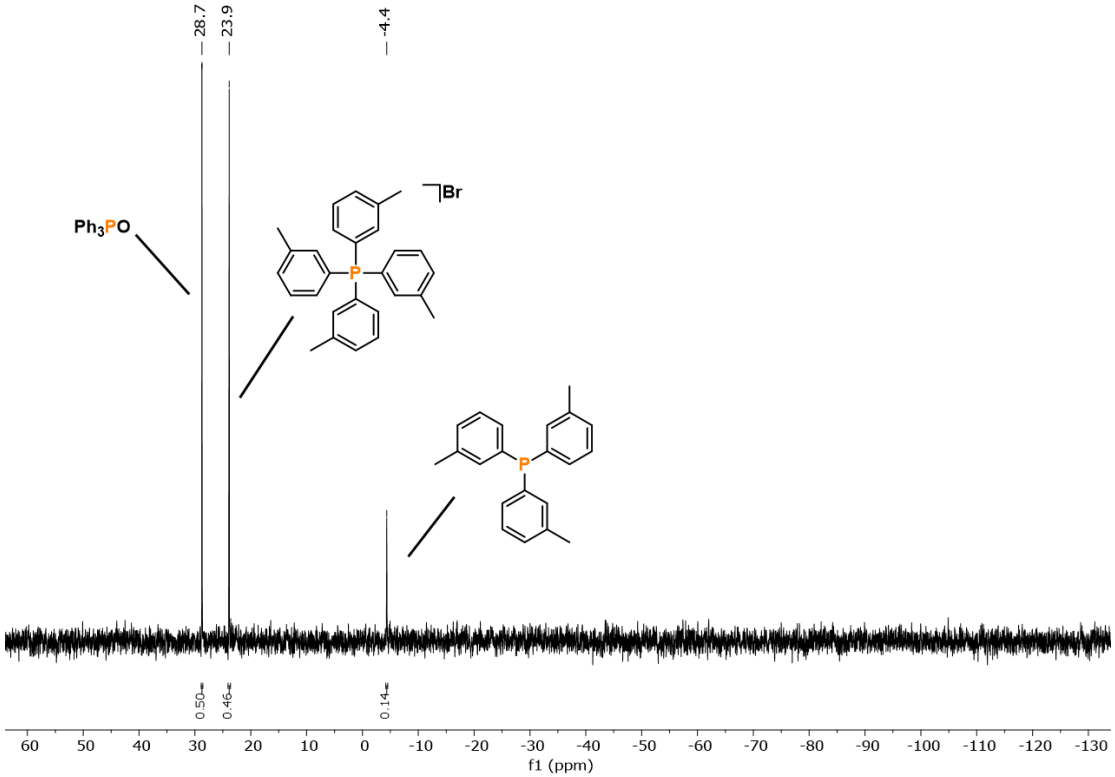


Figure S9. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-bromotoluene.

S4.1.8 Tris(*o*-tolyl)phosphine

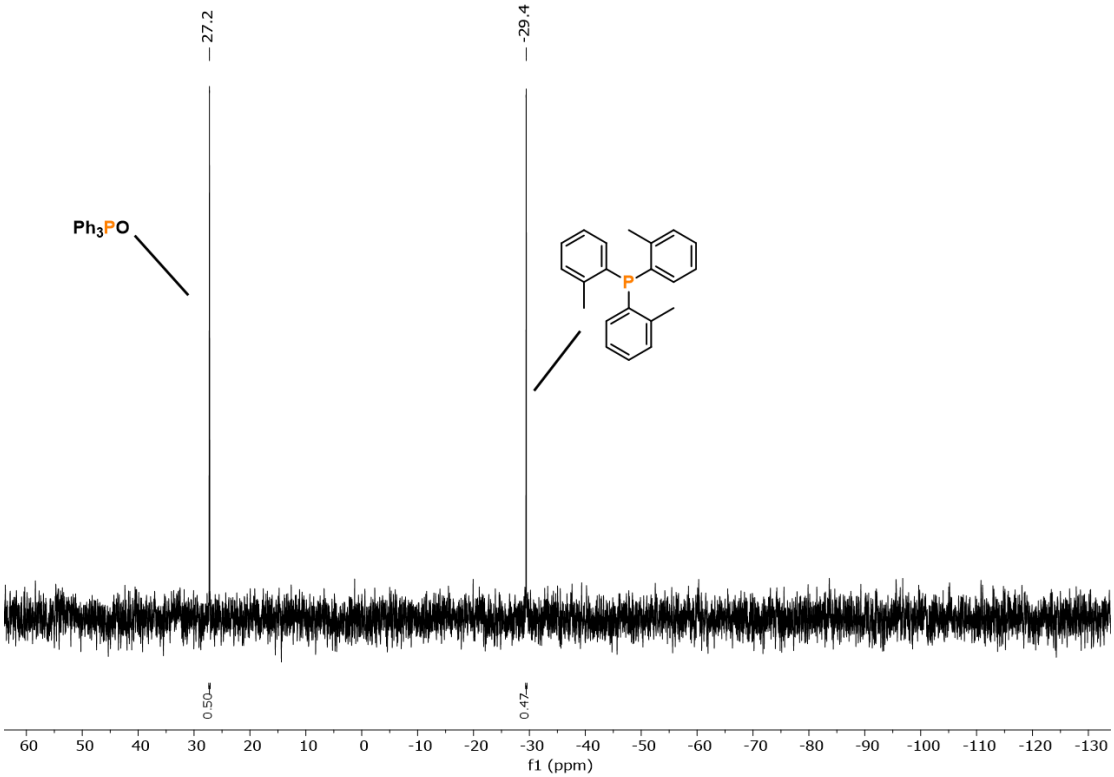


Figure S10. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 2-bromotoluene.

S4.1.9 Tetrakis(4-ethylphenyl)phosphonium bromide and tris(4-ethylphenyl)phosphine

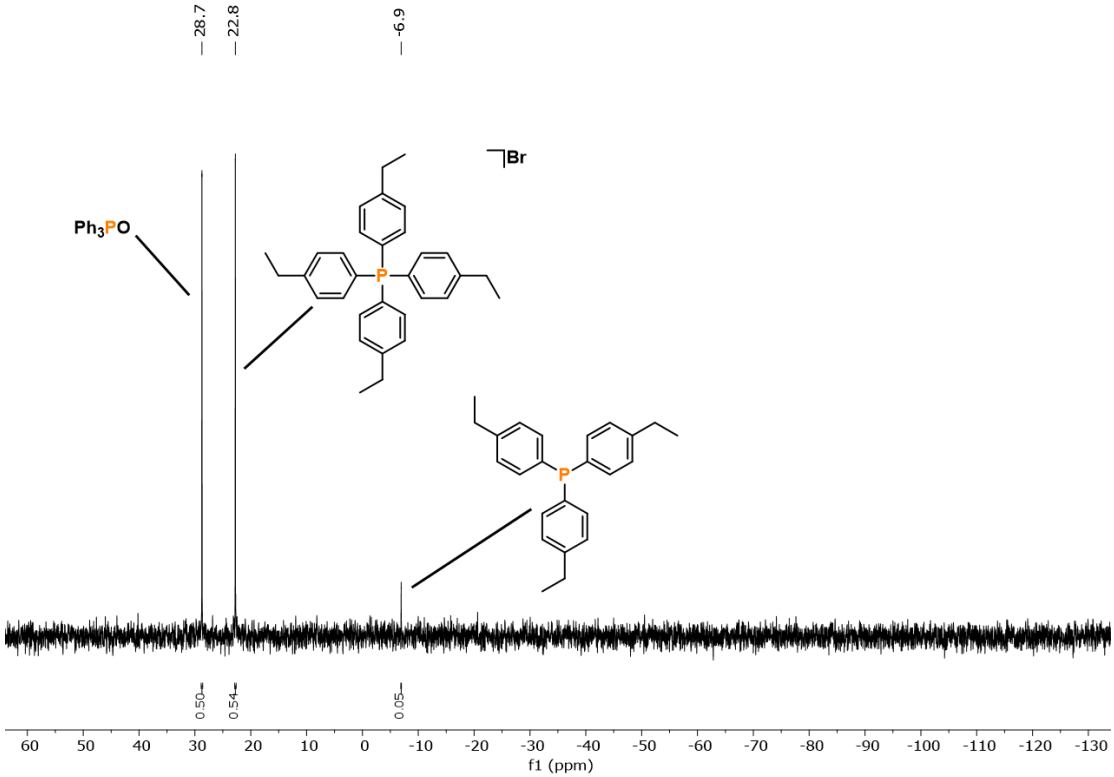


Figure S11. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-bromo-4-ethylbenzene.

S4.1.10 Tetrakis(3-ethylphenyl)phosphonium bromide and tris(3-ethylphenyl)phosphine[5]

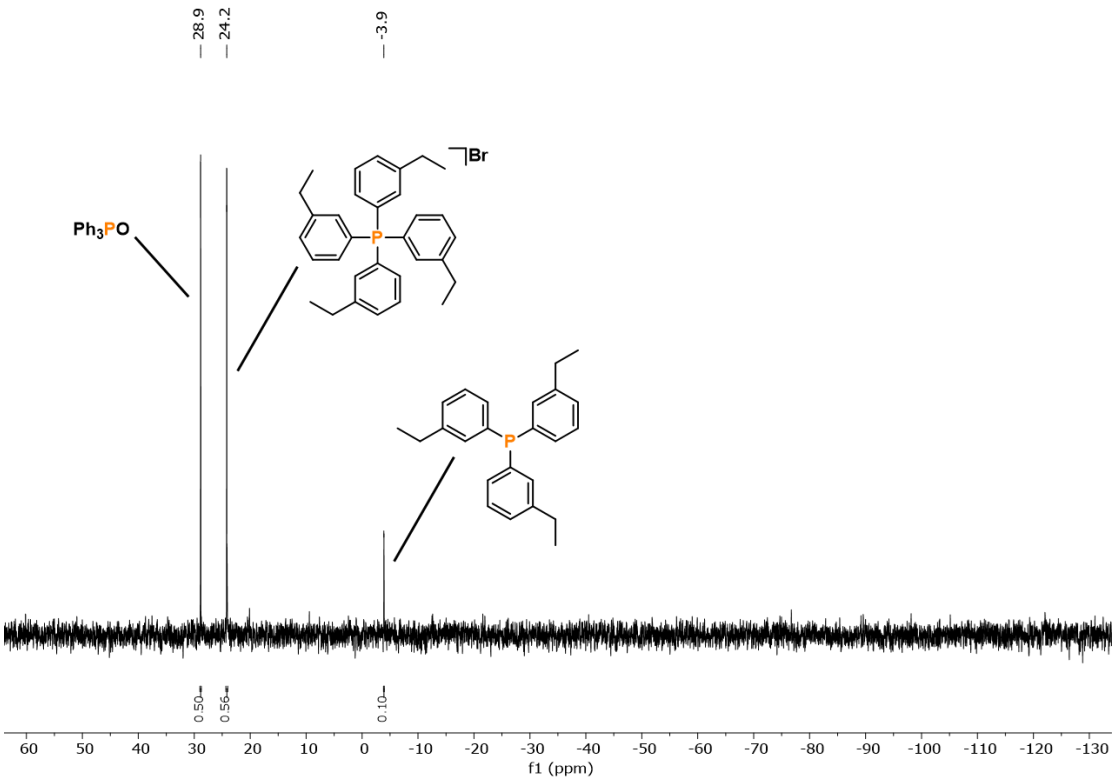


Figure S12. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-bromo-3-ethylbenzene.

S4.1.11 Tetrakis[(4-methylthio)phenyl]phosphonium bromide and tris[(4-methylthio)phenyl]-phosphine[6]

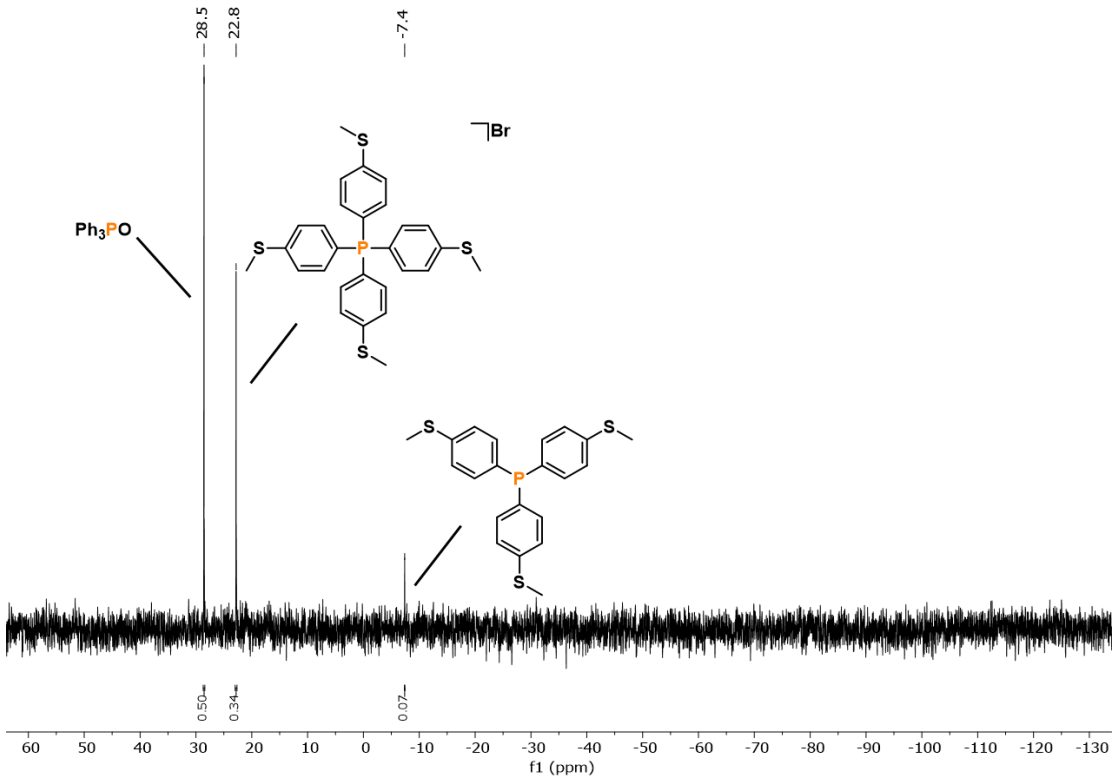


Figure S13. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-bromothioanisole.

S4.1.12 Tetrakis(4-phenoxyphenyl)phosphonium bromide and tris(4-phenoxyphenyl)phosphine[7]

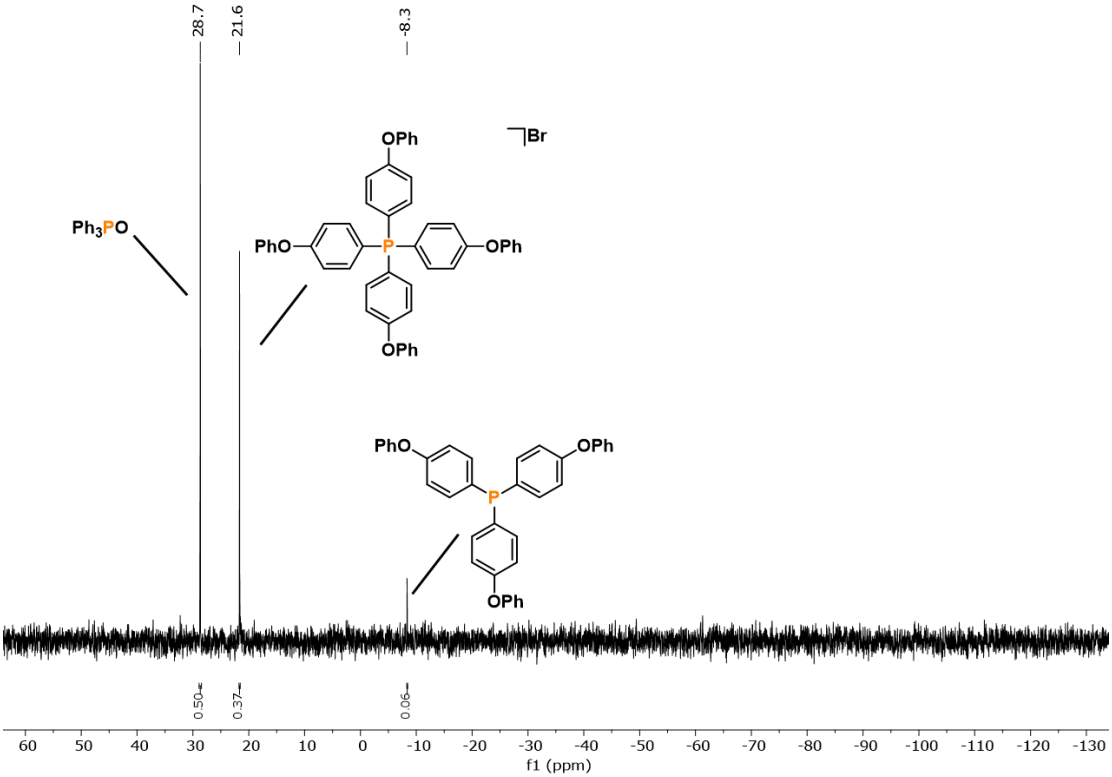


Figure S14. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-bromo-4-phenoxybenzene.

S4.1.13 Tetrakis[(4-*tert*-butyl)phenyl]phosphonium bromide and tris[(4-*tert*-butyl)phenyl]phosphine

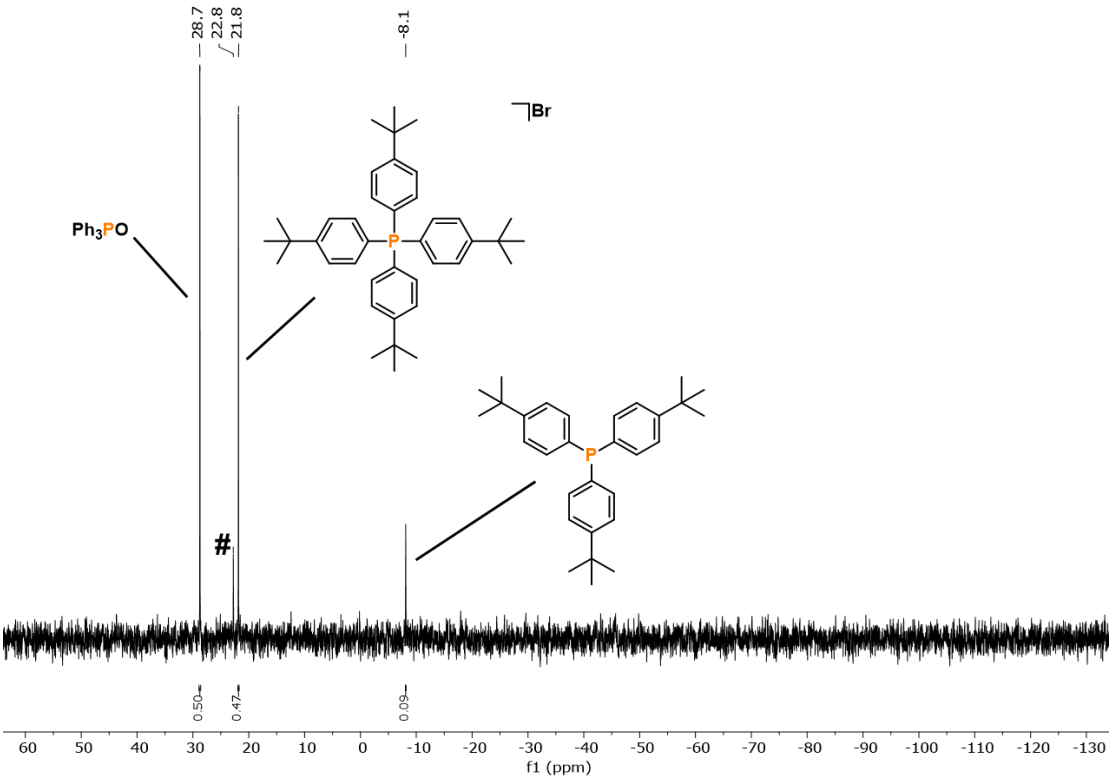


Figure S15. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-bromo-4-*tert*-butylbenzene. #: unidentified signal.

S4.1.14 Tetrakis(4-methyl benzoate)phosphonium bromide

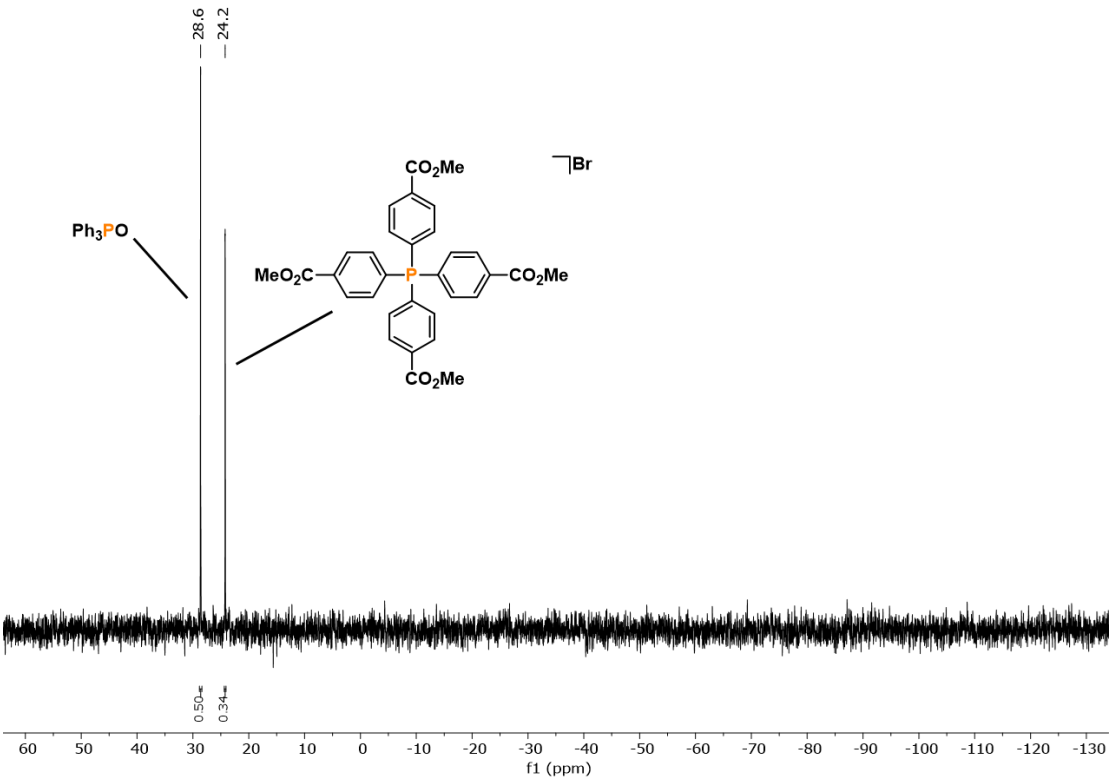


Figure S16. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using methyl 4-bromobenzoate.

S4.1.15 Tetrakis(3-methyl benzoate)phosphonium bromide and tris(3-methyl benzoate)phosphine

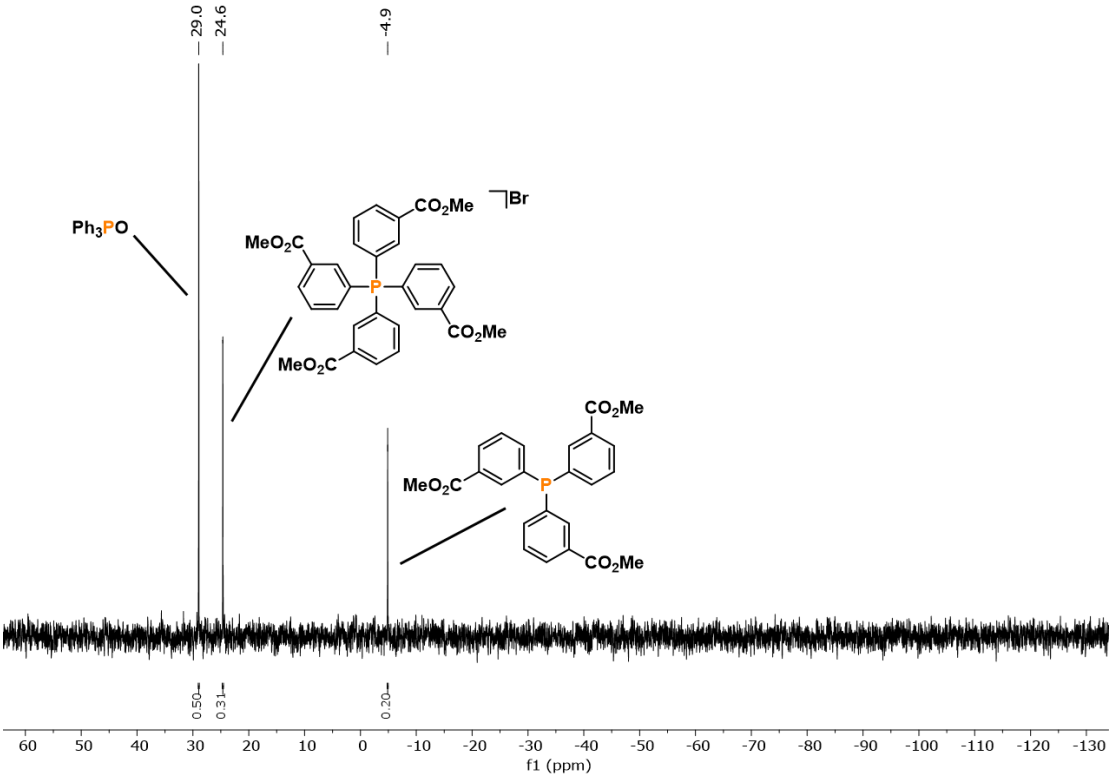


Figure S17. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using methyl 3-bromobenzoate.

S4.1.16 Tetrakis[(4-cyano)phenyl]phosphonium bromide and tris[(4-cyano)phenyl]phosphine[8]

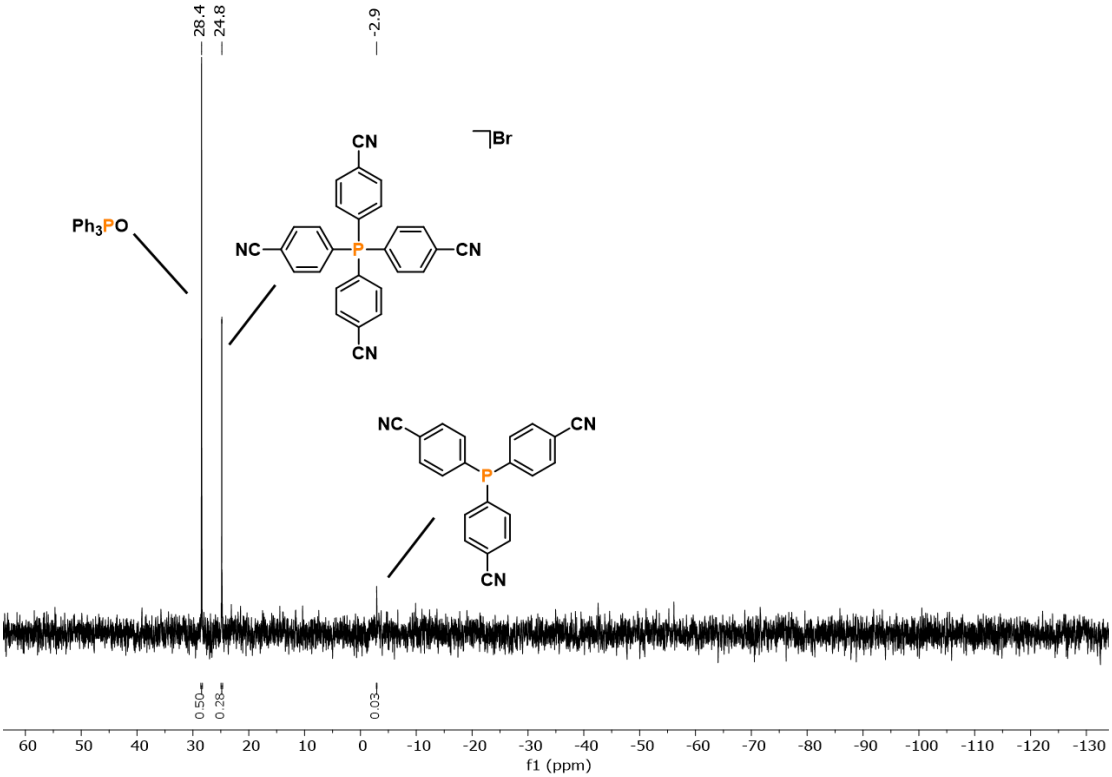


Figure S18. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-bromobenzonitrile.

S4.1.17 Tetrakis[(3-cyano)phenyl]phosphonium bromide and tris[(3-cyano)phenyl]phosphine[9]

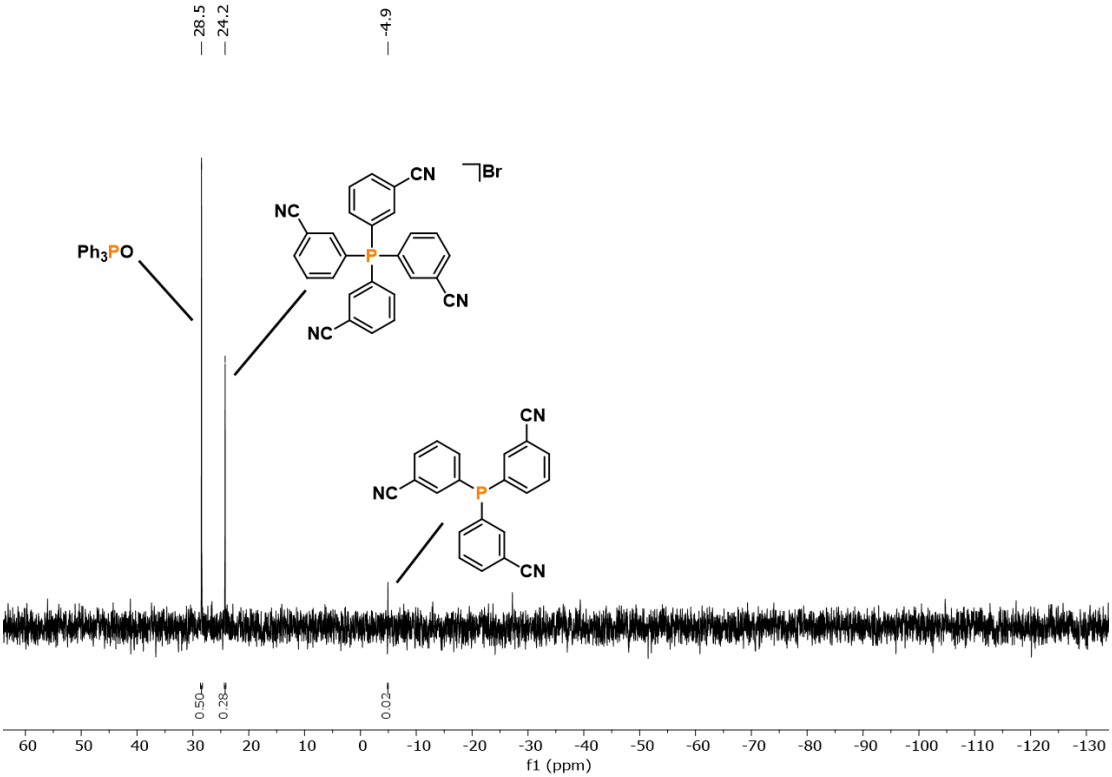


Figure S19. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-bromobenzonitrile.

S4.1.18 Tetrakis[(4-trifluoromethyl)phenyl]phosphonium bromide and tris[(4-trifluoromethyl)-phenyl]phosphine

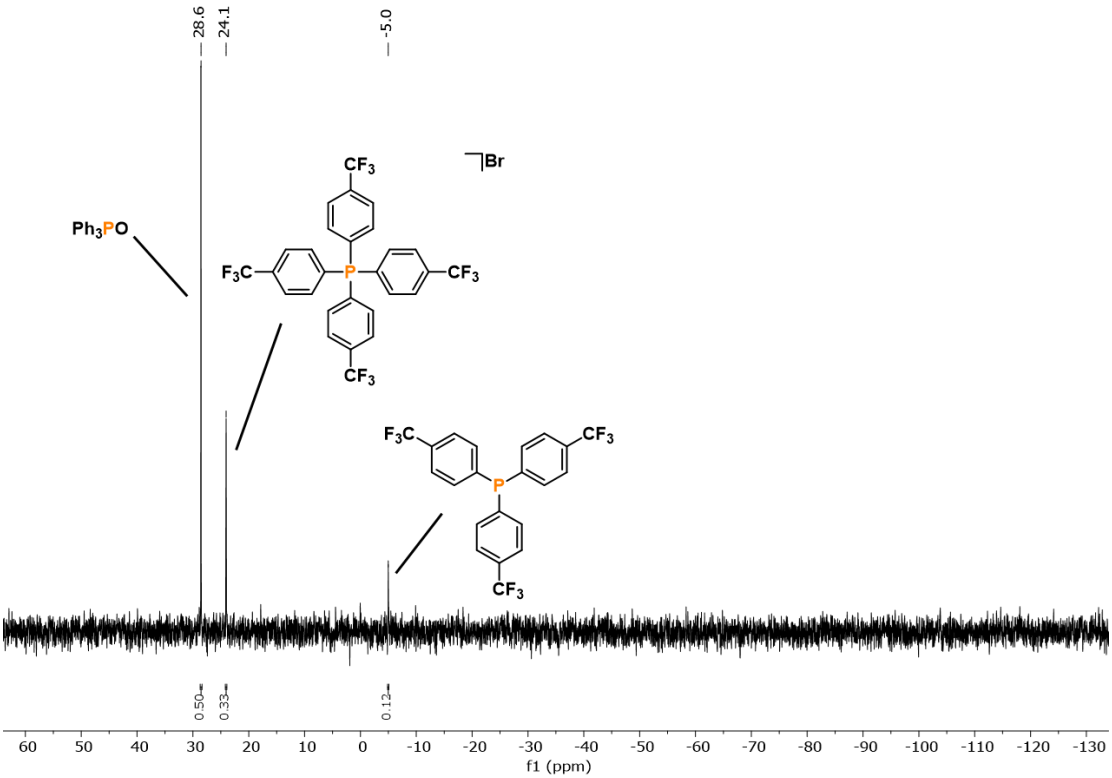


Figure S20. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-bromobenzotrifluoride.

S4.1.19 Tetrakis(pyridine-3-yl)phosphonium bromide and tris(pyridine-3-yl)phosphine

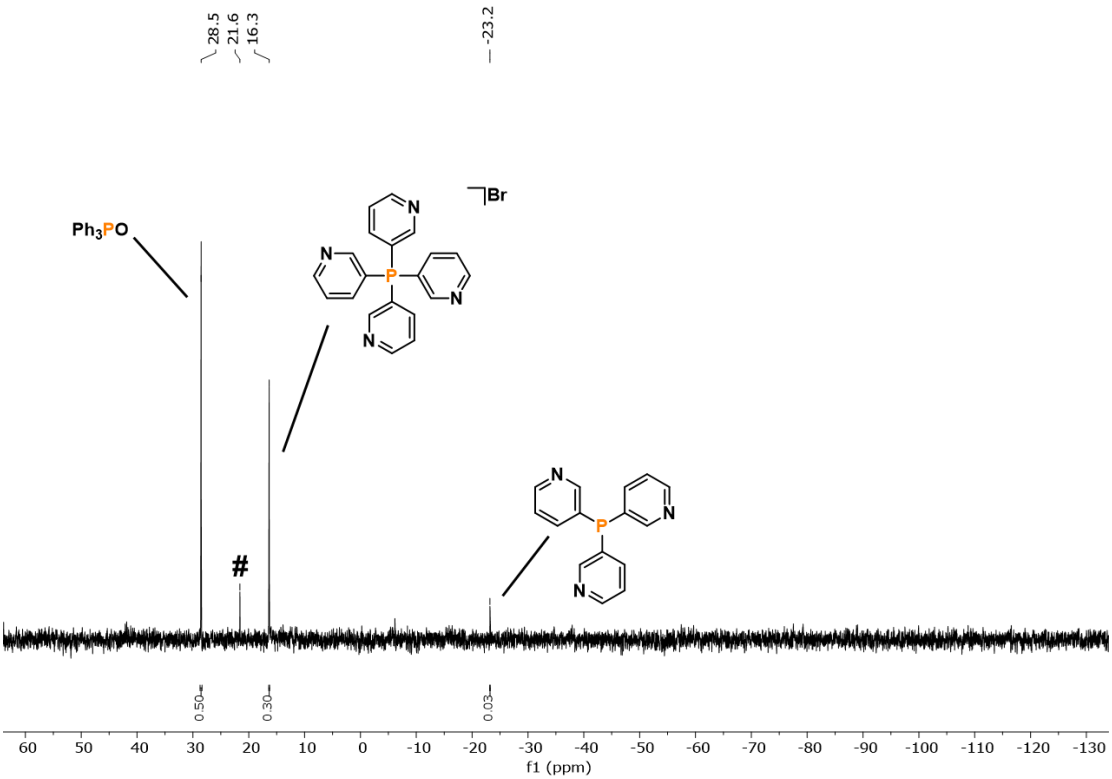


Figure S21. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-bromopyridine. #: unidentified signal.

Aryl chlorides – 44 h reaction time:

S4.1.20 Tetraphenylphosphonium chloride and triphenylphosphine

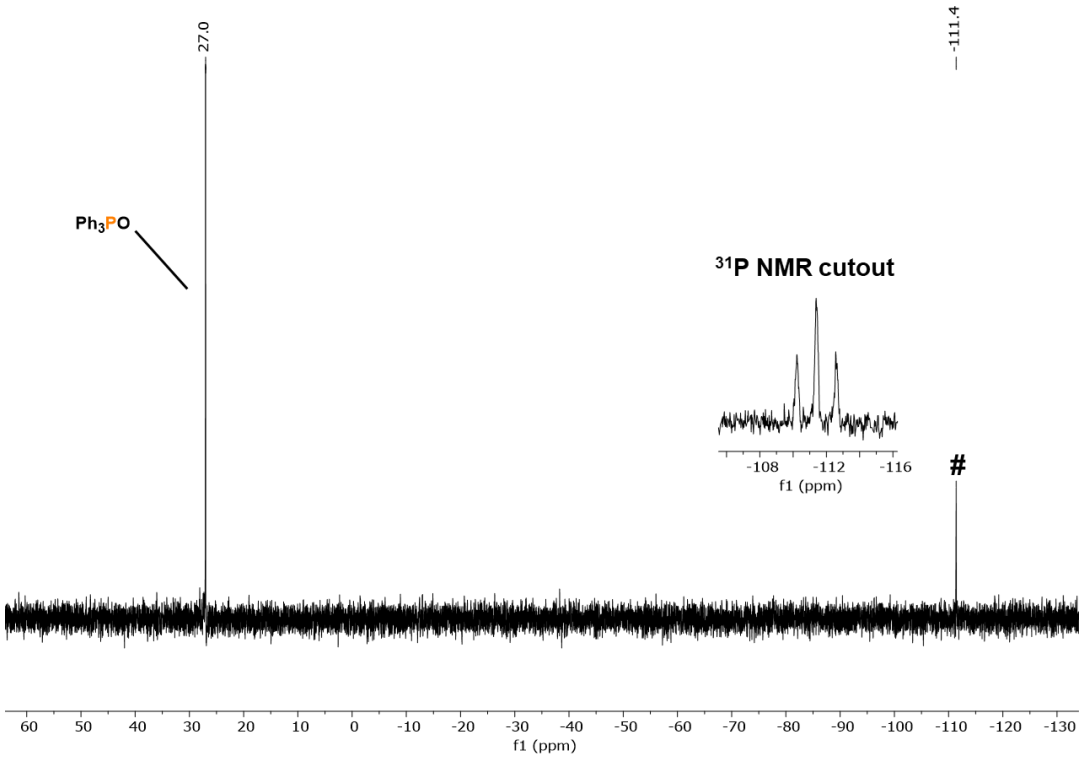


Figure S22. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using chlorobenzene. #: formation of $HPPh_2$ (assigned by ^{31}P NMR analysis, $^{1}J_{PH}$ = 188.9 Hz; shift of signal likely due to coordinative interactions).

S4.1.21 Tetra(4-methoxyphenyl)phosphonium chloride and tris(4-methoxyphenyl)phosphine

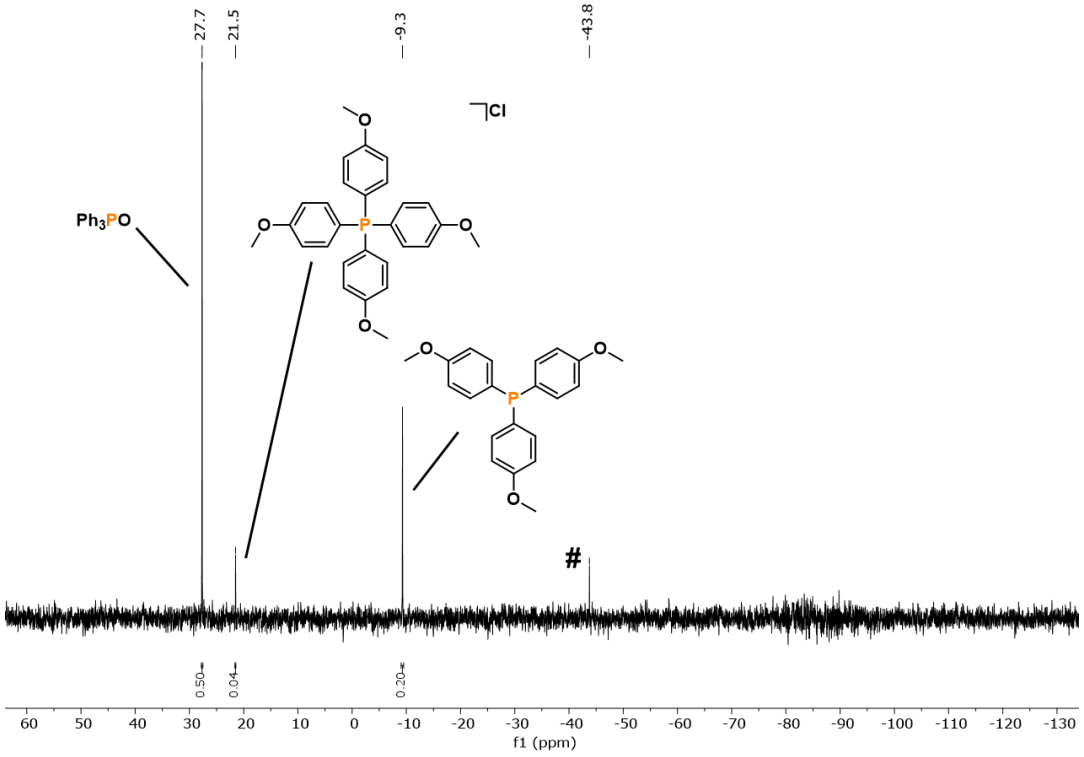


Figure S23. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-chloroanisole. #: di(*p*-methoxyphenyl)phosphine.

S4.1.22 Tetra(3-methoxyphenyl)phosphonium chloride and tris(3-methoxyphenyl)phosphine

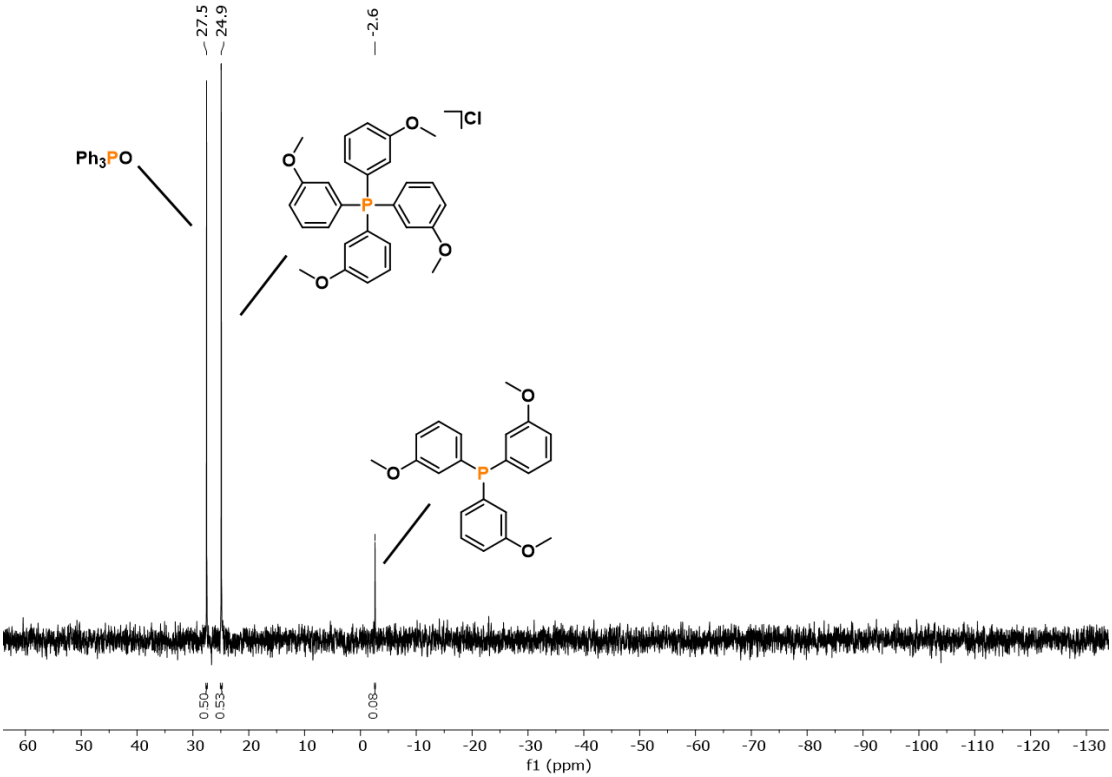


Figure S24. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-chloroanisole.

S4.1.23 Tris(2-methoxyphenyl)phosphine

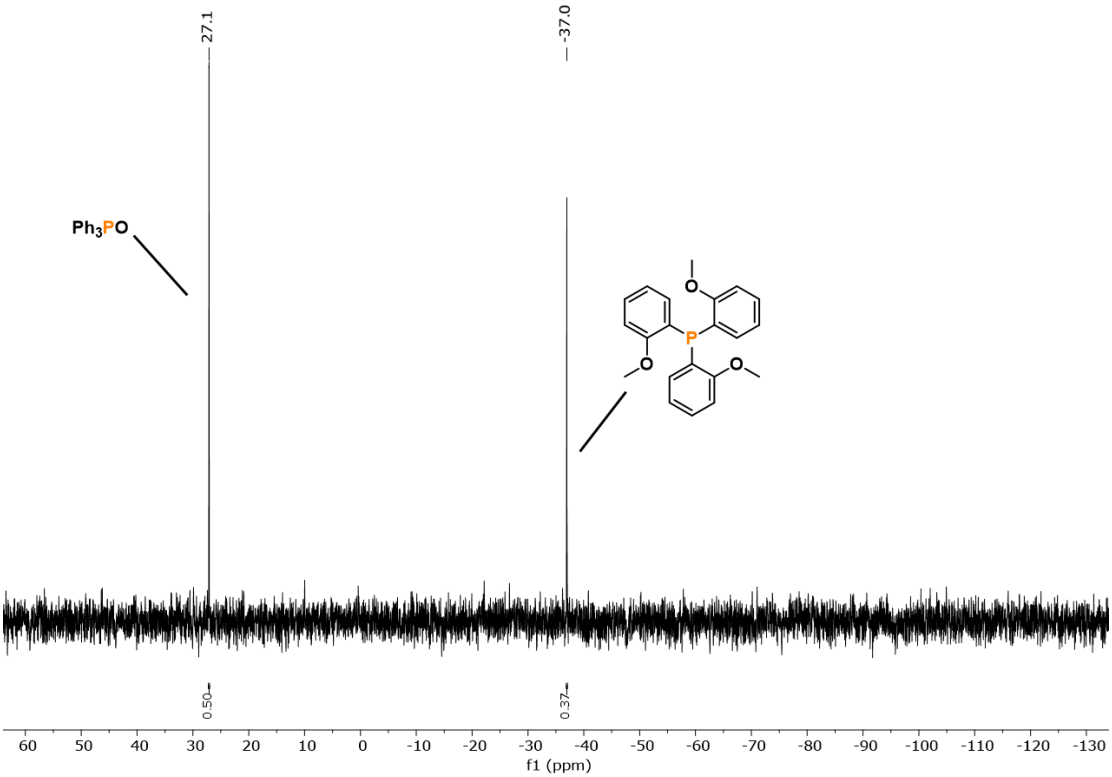


Figure S25. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 2-chloroanisole.

S4.1.24 Tetra(*p*-tolyl)phosphonium chloride and tris(*p*-tolyl)phosphine

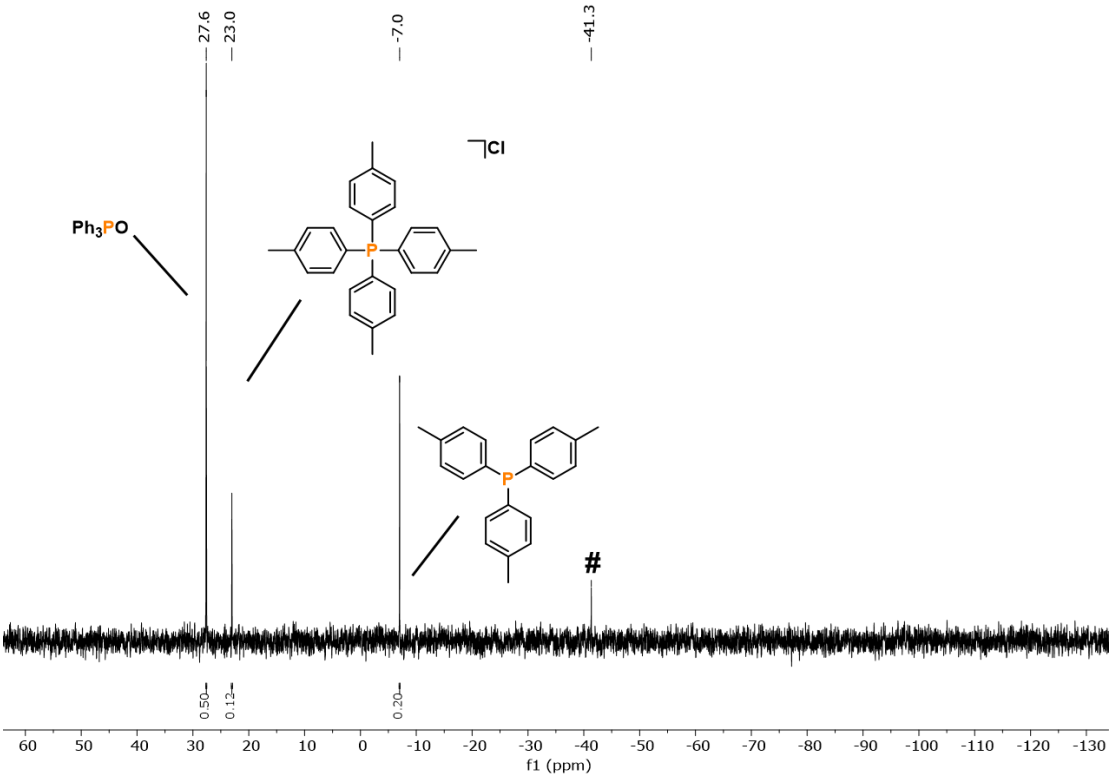


Figure S26. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-chlorotoluene. #: di(*p*-tolyl)phosphine.

S4.1.25 Tetra(*m*-tolyl)phosphonium chloride and tris(*m*-tolyl)phosphine

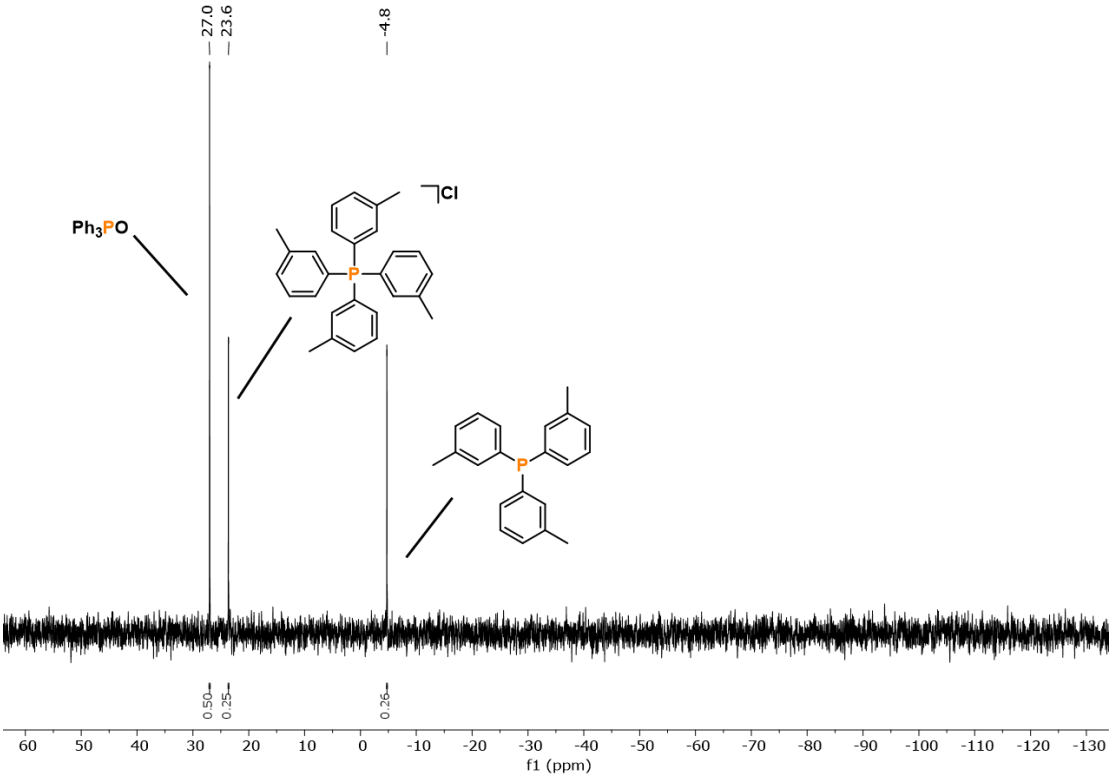


Figure S27. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-chlorotoluene.

S4.1.26 Tris(*o*-tolyl)phosphine

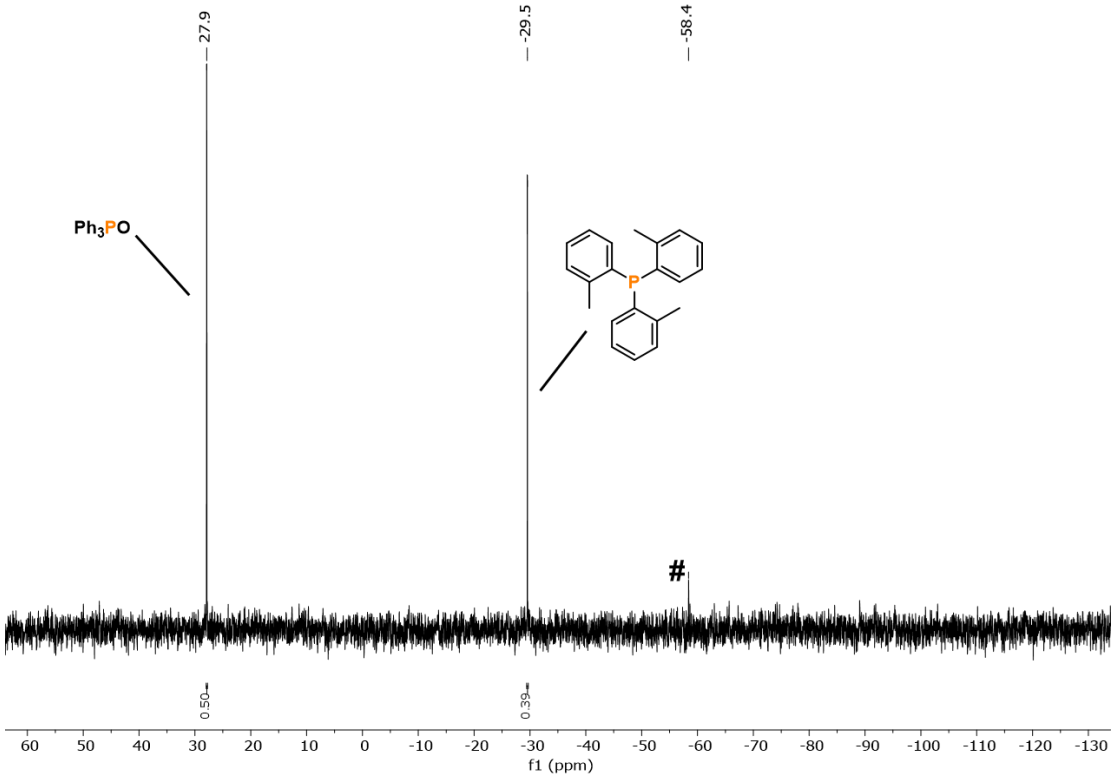


Figure S28. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 2-chlorotoluene. #: di(*o*-tolyl)phosphine.

S4.1.27 Tetrakis[(4-methylthio)phenyl]phosphonium chloride and tris[(4-methylthio)phenyl]phosphine[6]

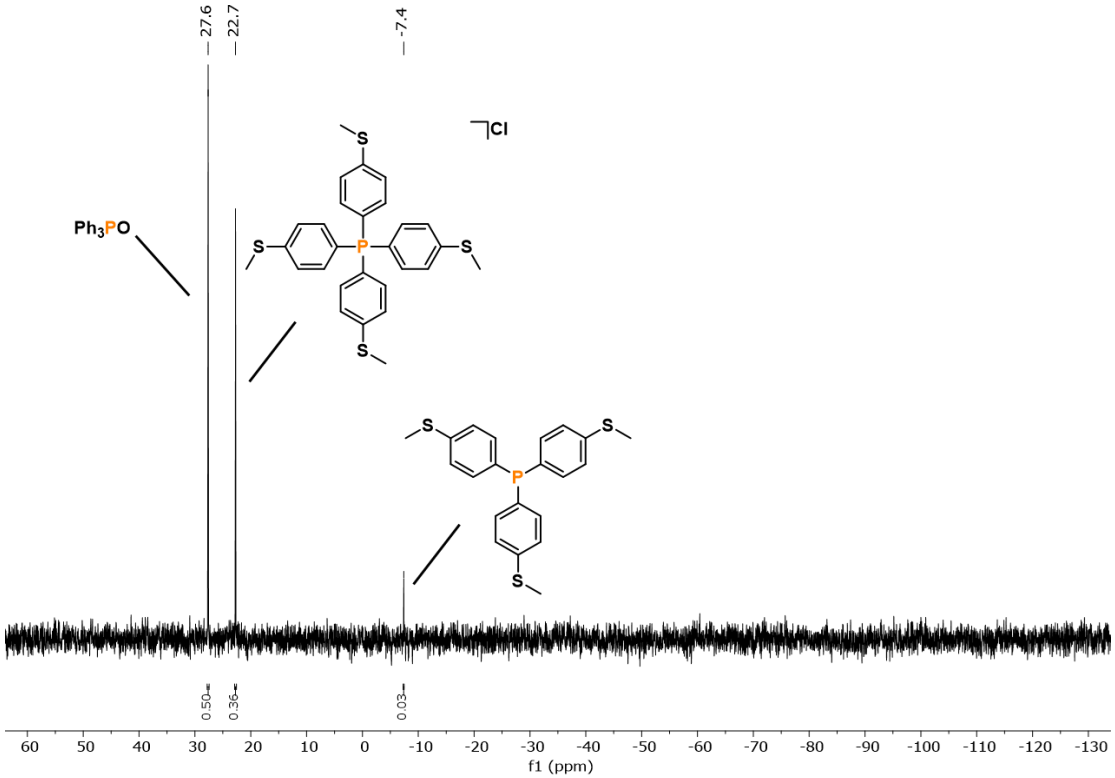


Figure S29. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-chlorothioanisole.

S4.1.28 Tetrakis(4-phenoxyphenyl)phosphonium chloride and tris(4-phenoxyphenyl)phosphine[7]

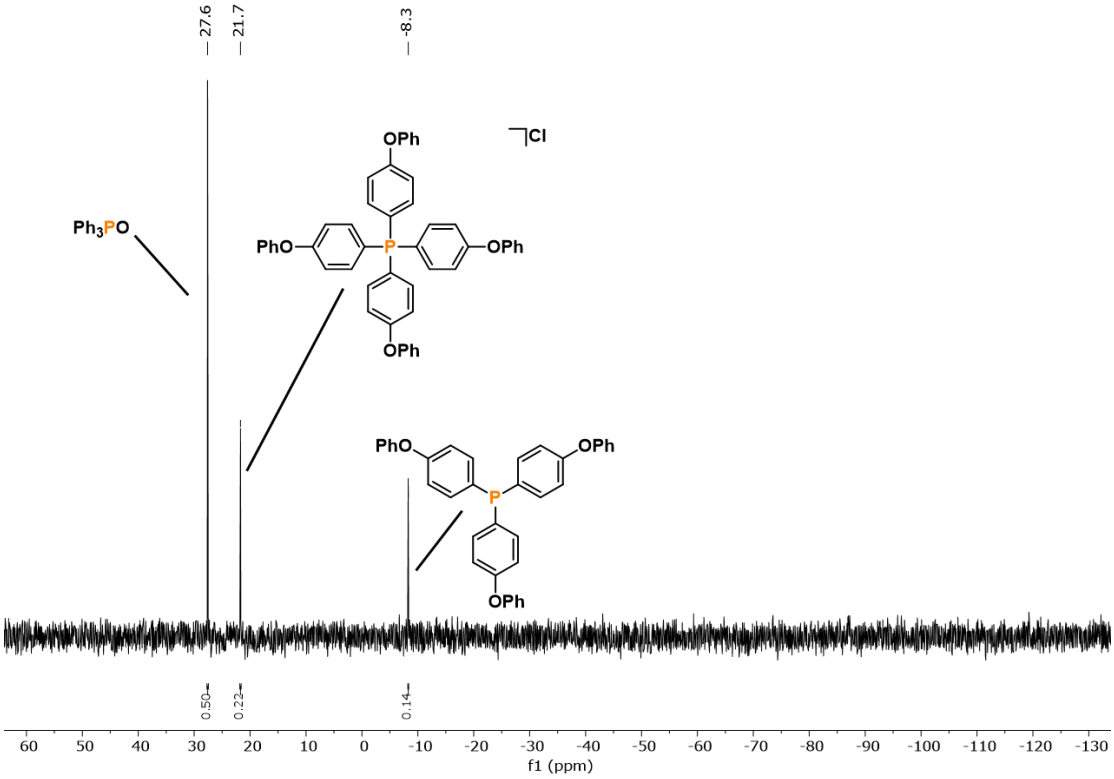


Figure S30. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-chloro-4-phenoxybenzene.

S4.1.29 Tetrakis(3,5-dimethoxyphenyl)phosphonium chloride and tris(3,5-dimethoxyphenyl)-phosphine[4]

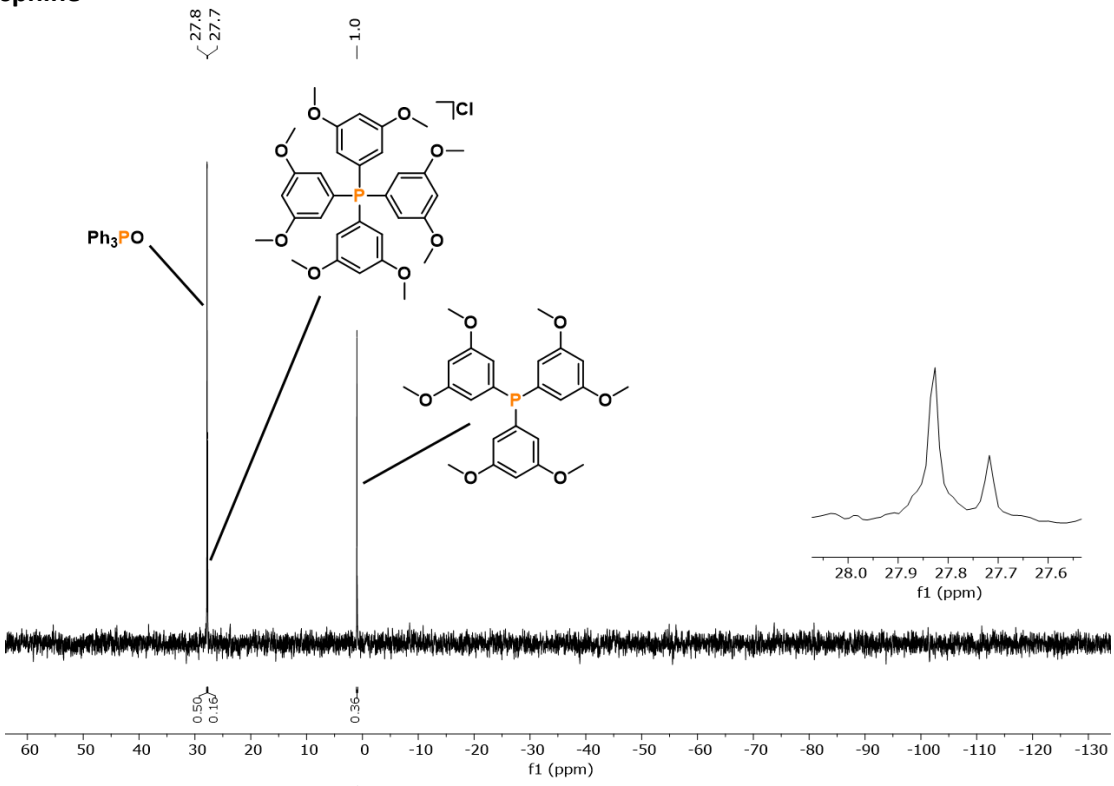


Figure S31. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-chloro-3,5-dimethoxybenzene.

S4.1.30 Tetrakis[(4-*tert*-butyl)phenyl]phosphonium chloride and tris[(4-*tert*-butyl)phenyl]phosphine

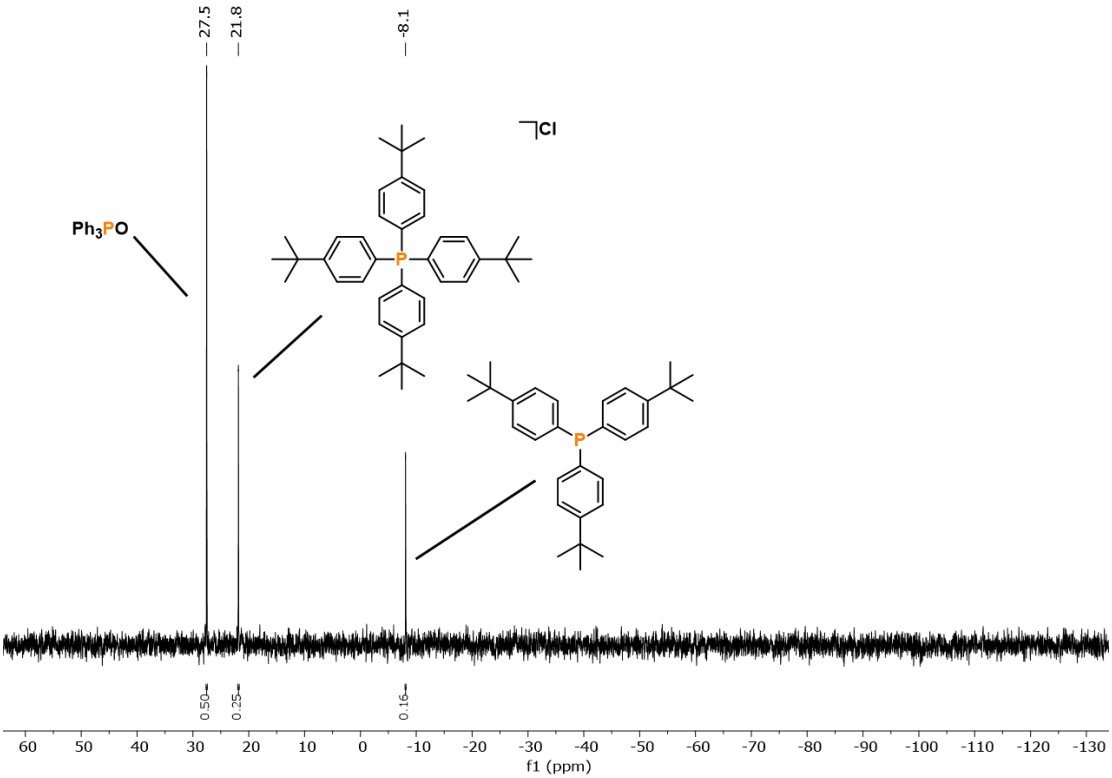


Figure S32. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-chloro-4-*tert*-butylbenzene.

S4.1.31 Tetrakis(4-ethylphenyl)phosphonium chloride and tris(4-ethylphenyl)phosphine

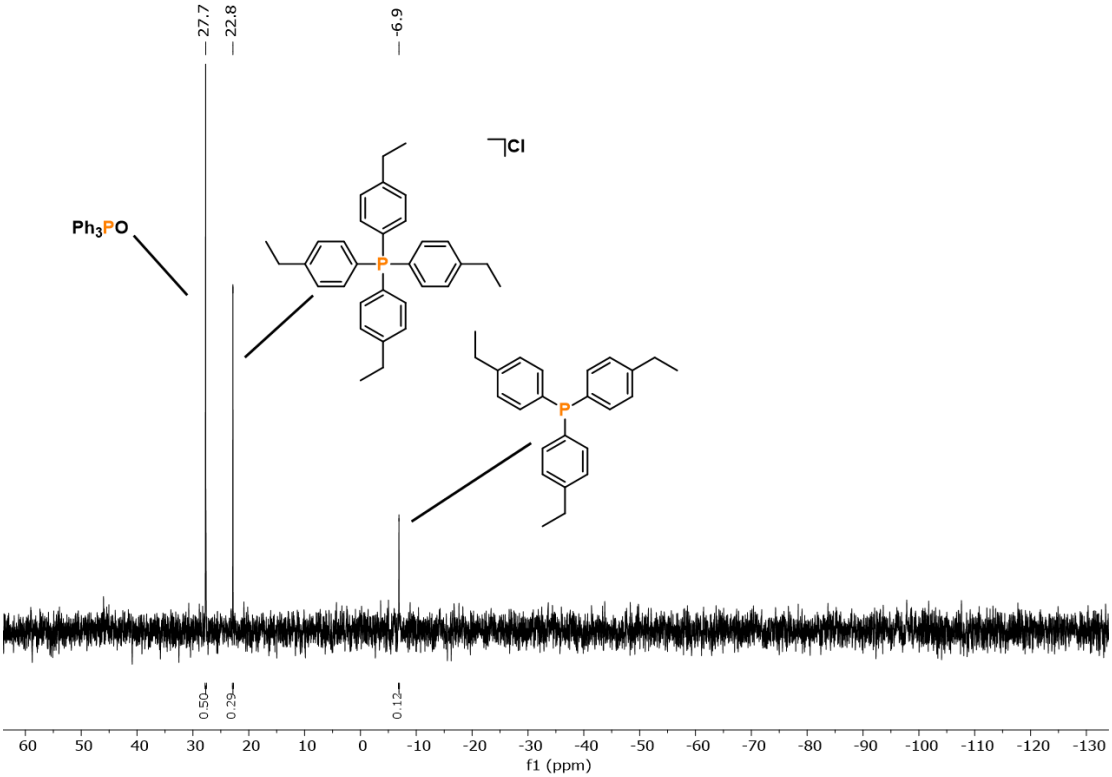


Figure S33. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-chloro-4-ethylbenzene.

S4.1.32 Tetrakis(3-ethylphenyl)phosphonium chloride and tris(3-ethylphenyl)phosphine[5]

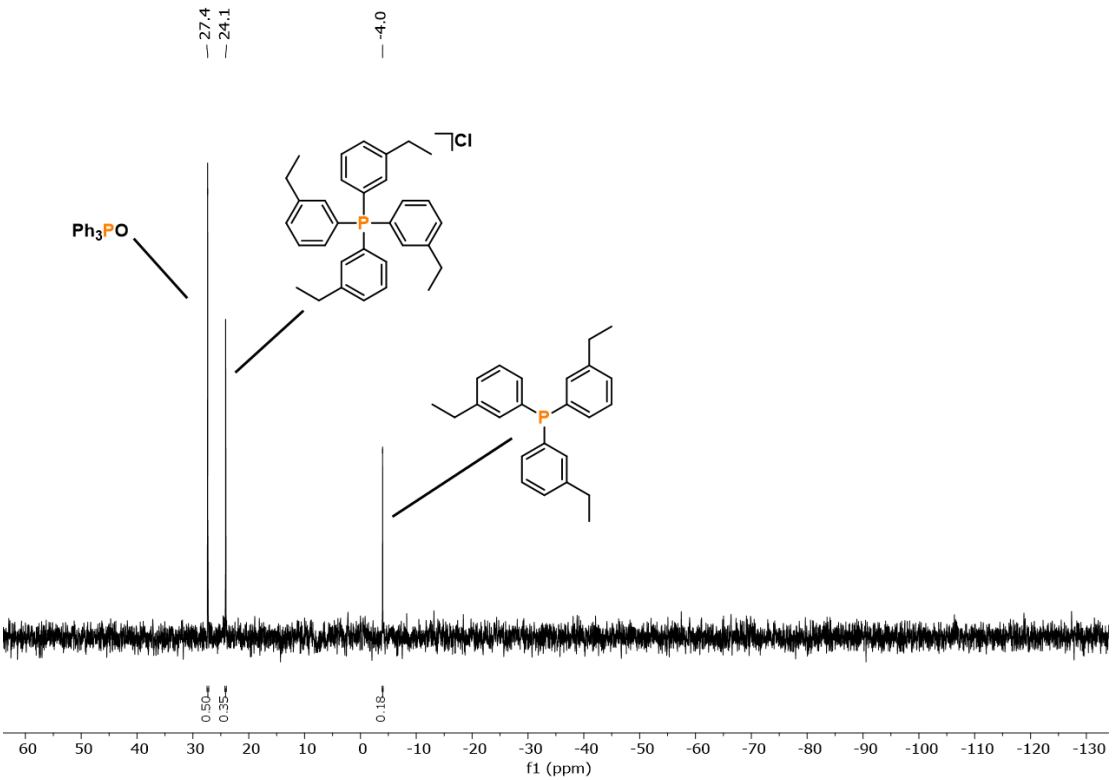


Figure S34. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-chloro-3-ethylbenzene.

S4.1.33 Tris[(4-cyano)phenyl]phosphine

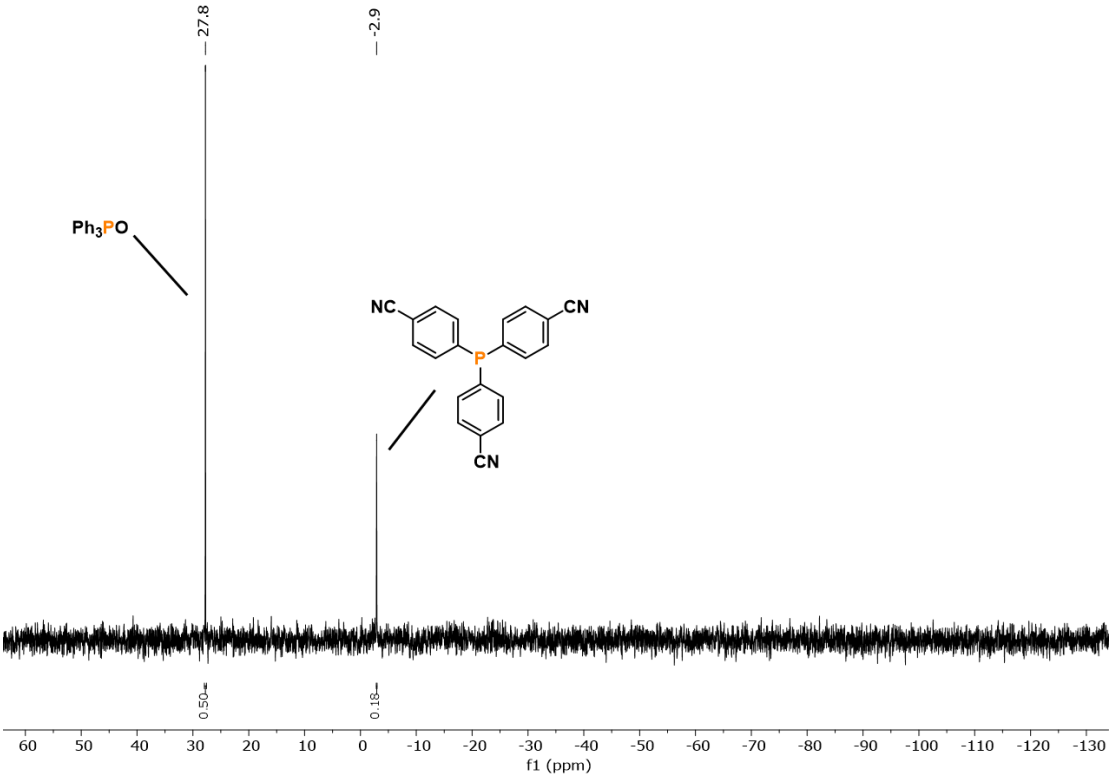


Figure S35. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-chlorobenzonitrile.

S4.1.34 Tetrakis[(3-cyano)phenyl]phosphonium chloride and tris[(3-cyano)phenyl]phosphine[8]

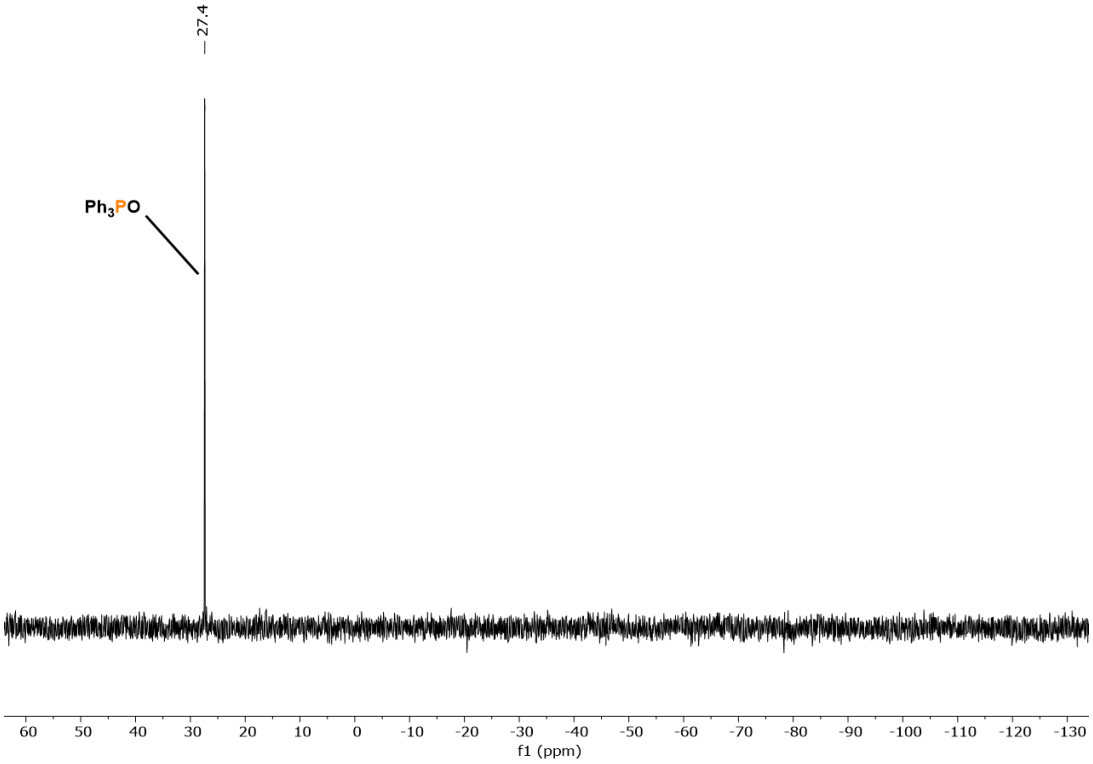


Figure S36. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-chlorobenzonitrile.

S4.1.35 Tris(4-methyl benzoate)phosphine

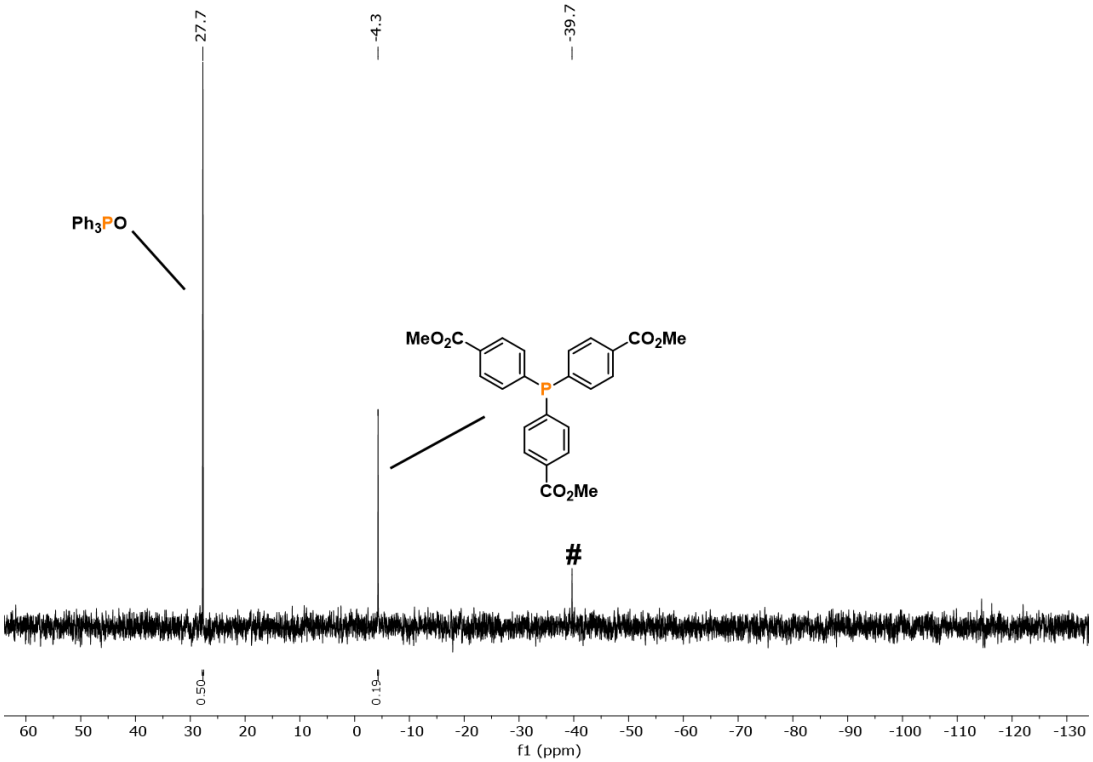


Figure S37. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using methyl 4-chlorobenzoate. #: Ar_2PH; Ar = 4-methylcarboxyphenyl.

S4.1.36 Tetrakis(3-methyl benzoate)phosphonium chloride and tris(3-methyl benzoate)phosphine

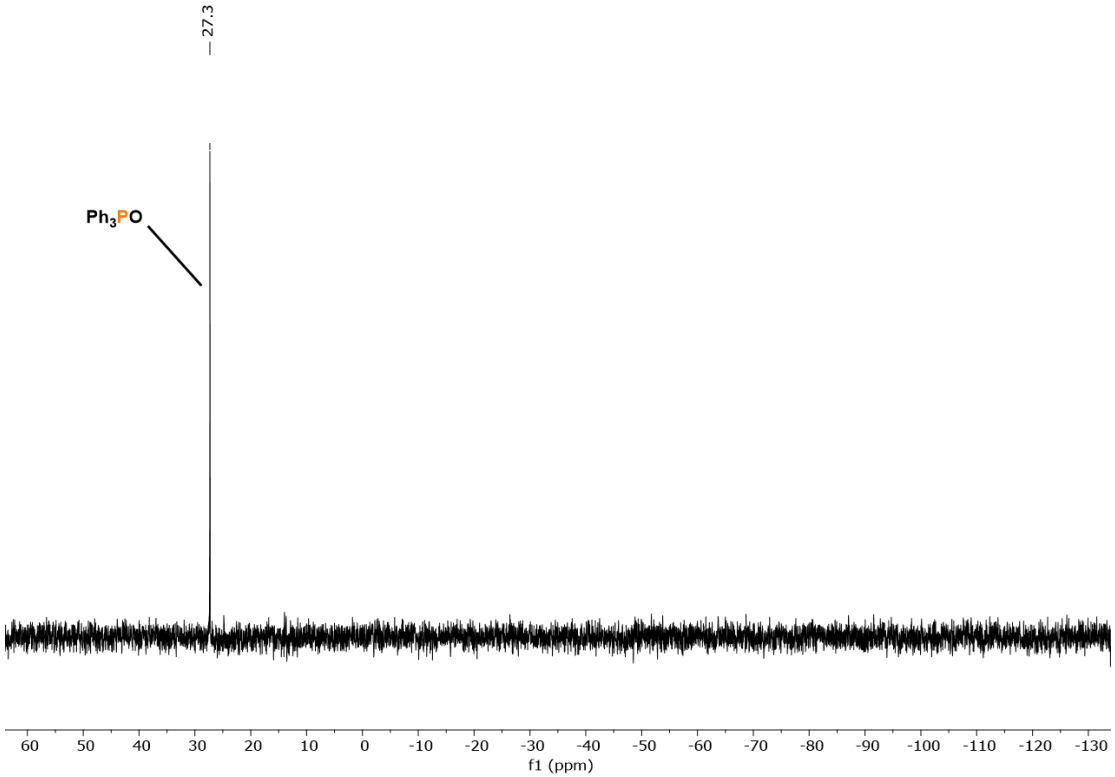


Figure S38. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using methyl 3-chlorobenzoate.

S4.1.37 Tris[(4-trifluoromethyl)-phenyl]phosphine

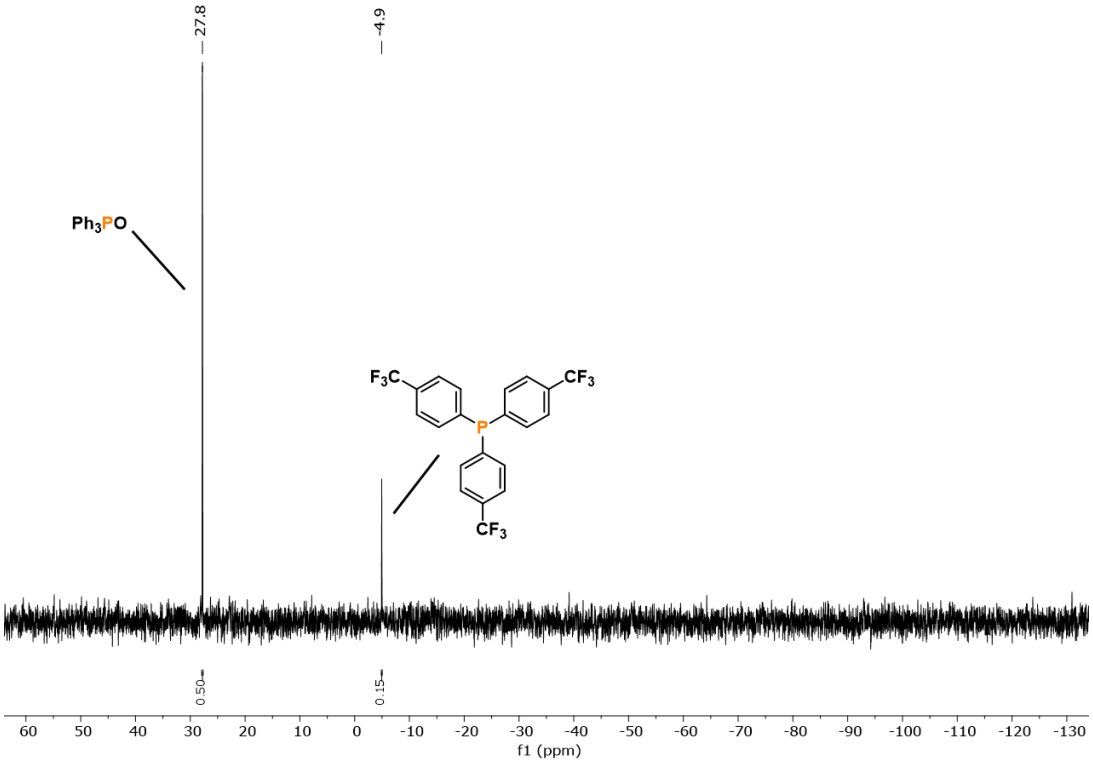


Figure S39. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-chlorobenzotrifluoride.

S4.1.38 Tetraphenylphosphonium halide (X = Br, Cl) from 1-bromo-4-chlorobenzene

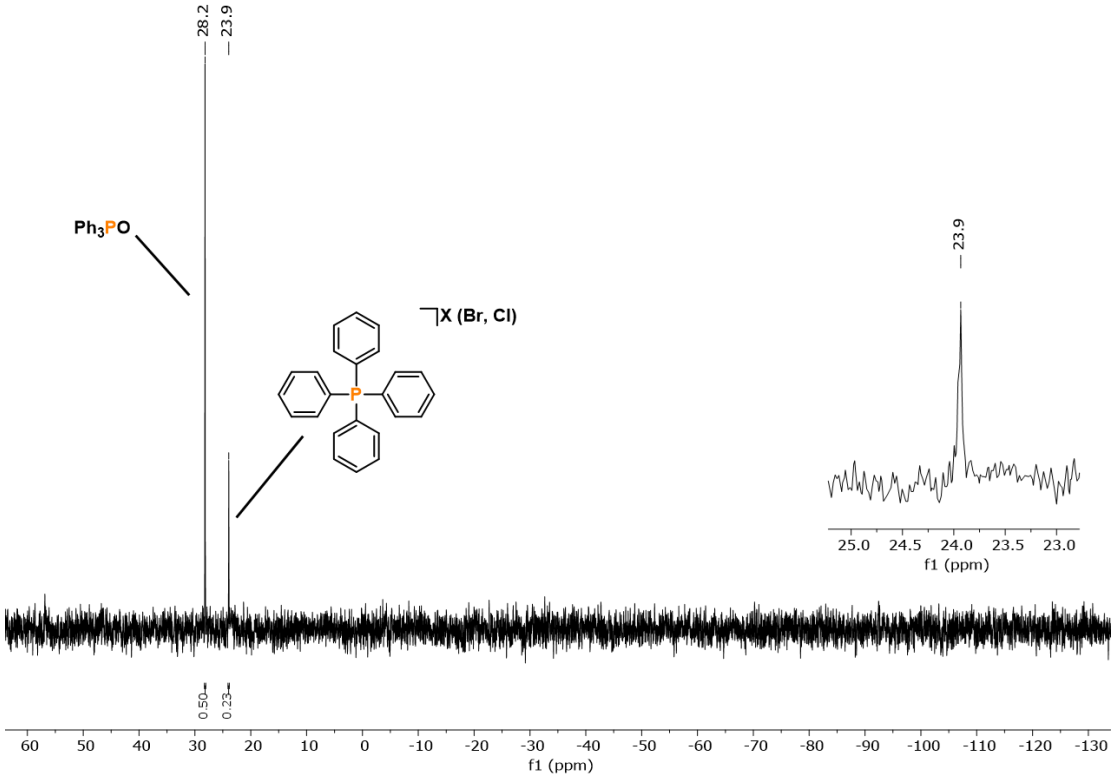


Figure S40. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-bromo-4-chlorobenzene. The cutout shows the exclusive formation of $[Ph_4P]X$ (X = Br, Cl).

S4.1.39 Tetrakis(pyridine-3-yl)phosphonium chloride and tris(pyridine-3-yl)phosphine

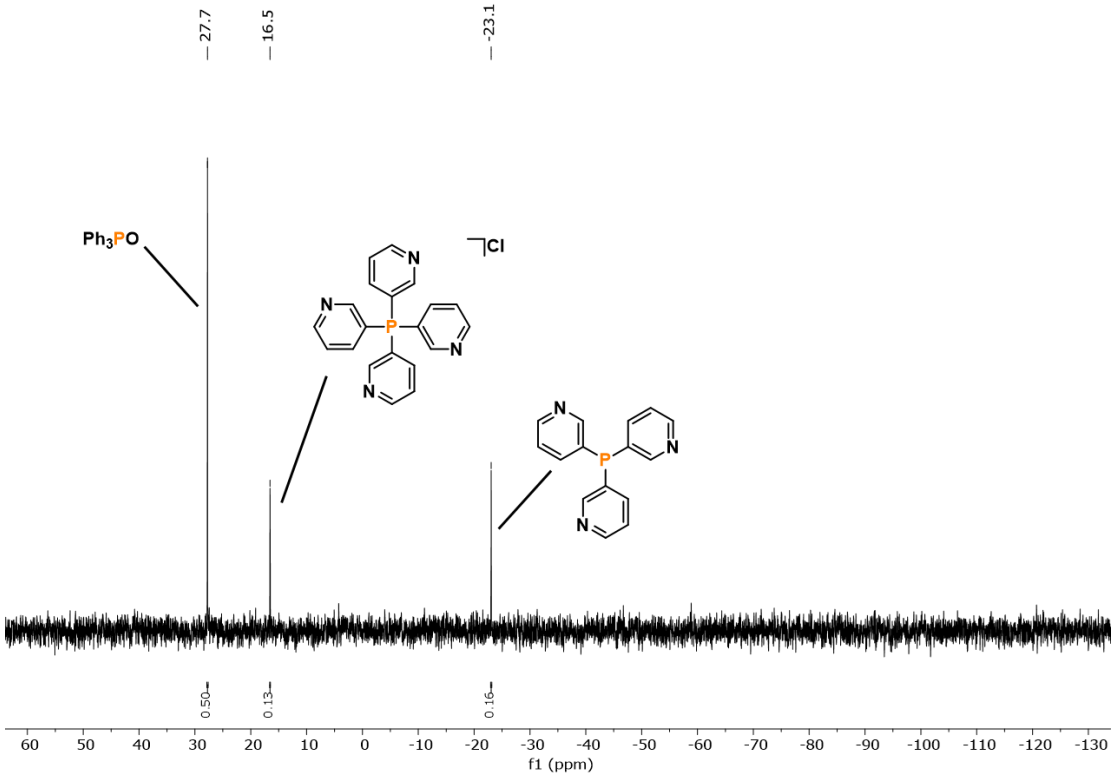
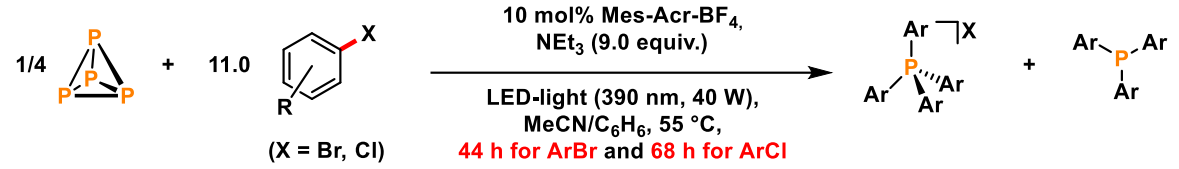
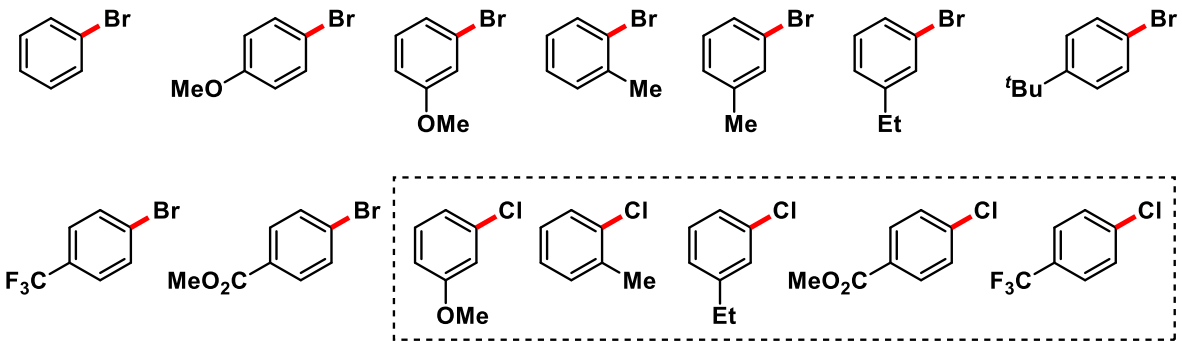


Figure S41. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-chloropyridine.

S4.2. $^{31}P\{^{1}H\}$ NMR spectroscopic data for aryl bromides after 44 h and aryl chlorides after 68 h reaction time

Table S11. Photocatalytic functionalization of P_4 to $[Ar_4P]X$ (X = Br, Cl) and Ar_3P: extended reaction times.[a]





Entry	Substrate		Full conv. of P_4?	Form. of $[Ar_4P]X$ / %	Form. of Ar_3P / %
	X	R			
1	Br	R = H	✓	64	0
2	Br	R = 4-OMe	✓	54	7
3	Br	R = 3-OMe	✓	51	20
4	Br	R = 2-Me	✓	0	50
5	Br	R = 3-Me	✓	60	15
6	Br	R = 3-Et	✓	62	8
7	Br	R = 4-^{t}Bu	✓	53	9
8	Br	R = 4-CF_3	✓	32	12
9	Br	R = 4-CO_2Me	✓	47	0
10	Cl	R = 3-OMe	✓	62	11
11	Cl	R = 2-Me	✓	0	44
12	Cl	R = 3-Et	✓	59	13
13	Cl	R = 4-CO_2Me	✓	0	29
14	Cl	R = 4-CF_3	✓	0	16

[a] For the general procedure, see section S2. The reaction time was extended to 44 h for aryl bromides and to 68 h for aryl chlorides.

The screening of different aryl bromides and chlorides for extended reaction times (for X = Br: 44 h and X = Cl: 68 h) shows that the product formation ($[Ar_4P]X/Ar_3P$) can be noticeably improved (e.g. combined 71% $[Ar_4P]Br/Ar_3P$ starting from 3-bromoanisole or combined 73% $[Ar_4P]Cl/Ar_3P$ starting from 3-chloroanisole instead of 60% $[Ar_4P]Br/Ar_3P$ or 61% $[Ar_4P]Cl/Ar_3P$, respectively; see Table S10). Yet, prolonged reaction times were not found to be beneficial for all haloarenes, as indicated by the

similar NMR yields for bromobenzene (63% vs. 64%) or 2-chlorotoluene (39% vs. 44%). A general correlation between extended reaction times and improved yields was not observed.

Aryl bromides – 44 h reaction time:

S4.2.1 Tetraphenylphosphonium bromide

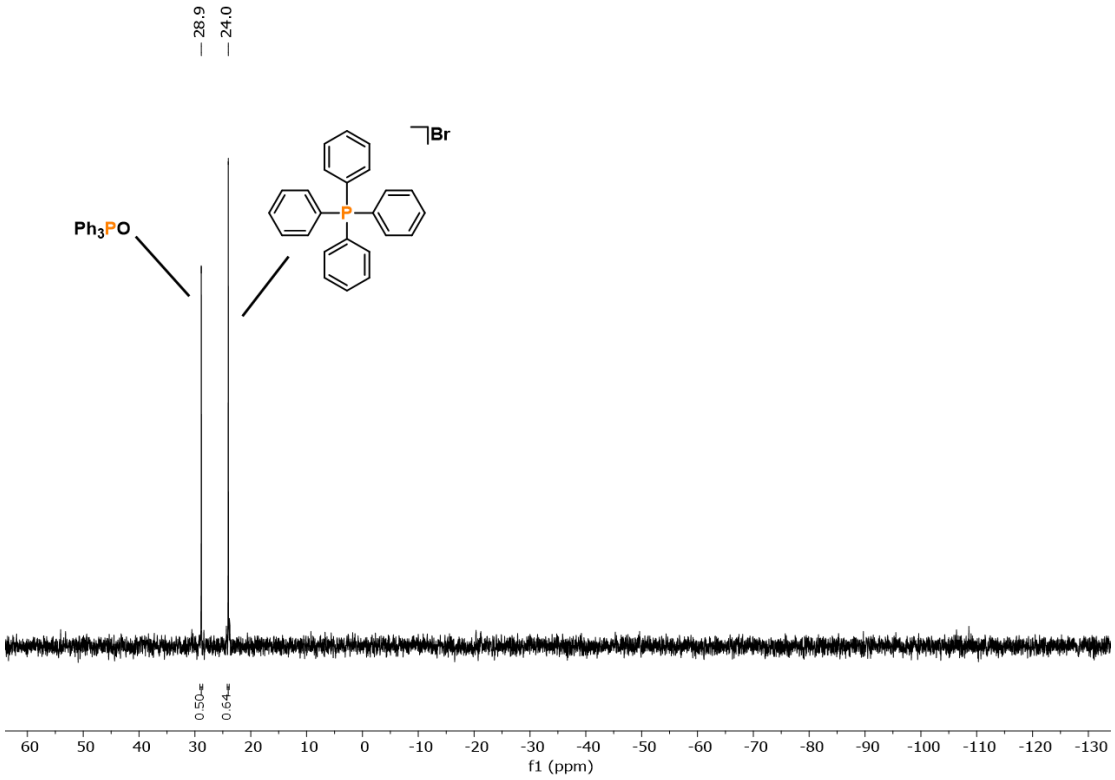


Figure S42. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using bromobenzene after 44 h reaction time.

S4.2.2 Tetrakis(4-methoxyphenyl)phosphonium bromide and tris(4-methoxyphenyl)phosphine

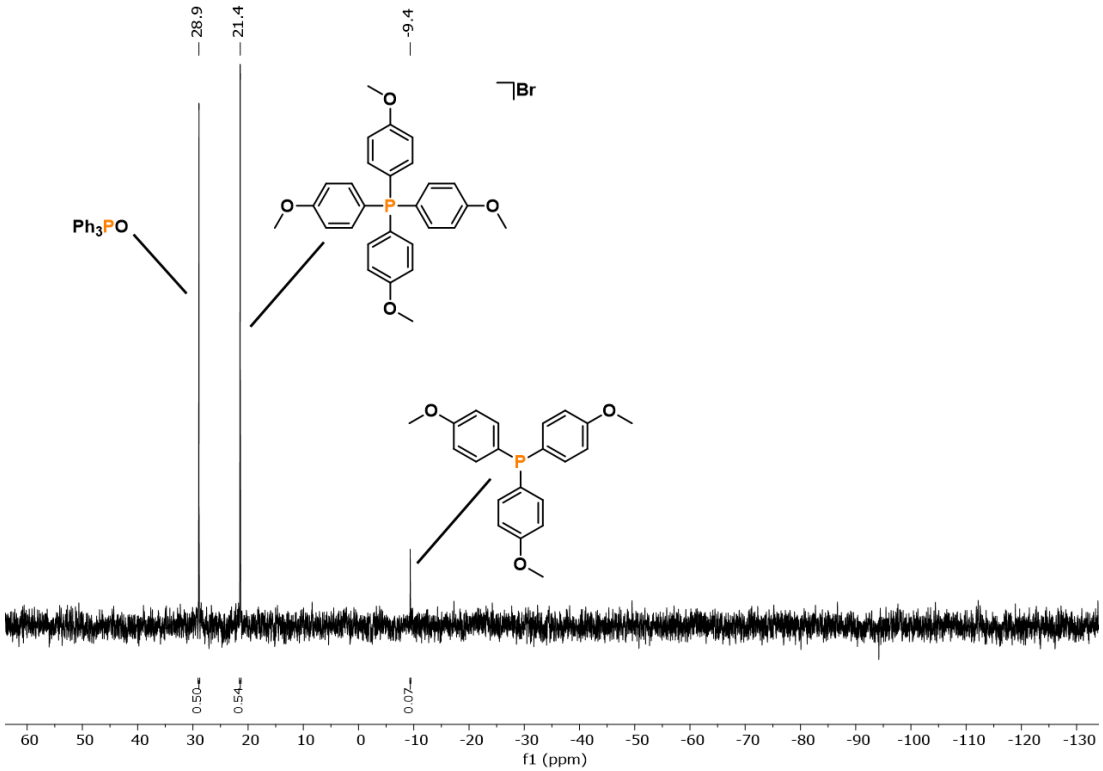


Figure S43. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-bromoanisole after 44 h reaction time.

S4.2.3 Tetrakis(3-methoxyphenyl)phosphonium bromide and tris(4-methoxyphenyl)phosphine

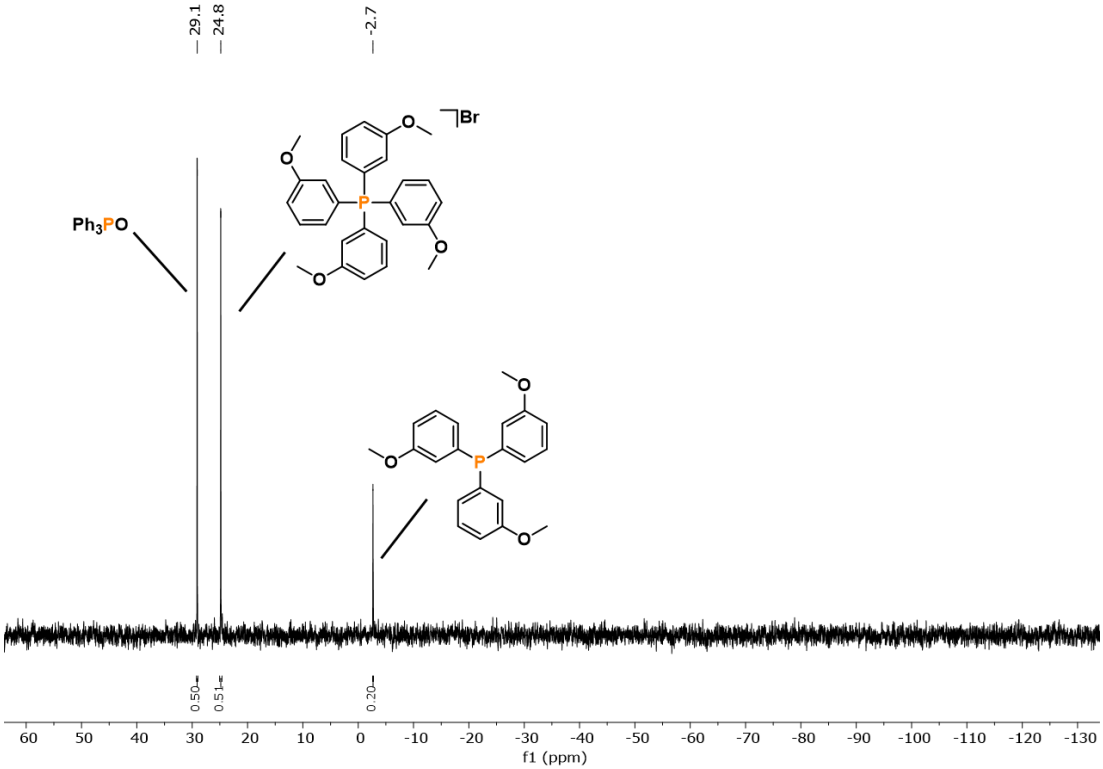


Figure S44. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-bromoanisole after 44 h reaction time.

S4.2.4 Tris(*o*-tolyl)phosphine

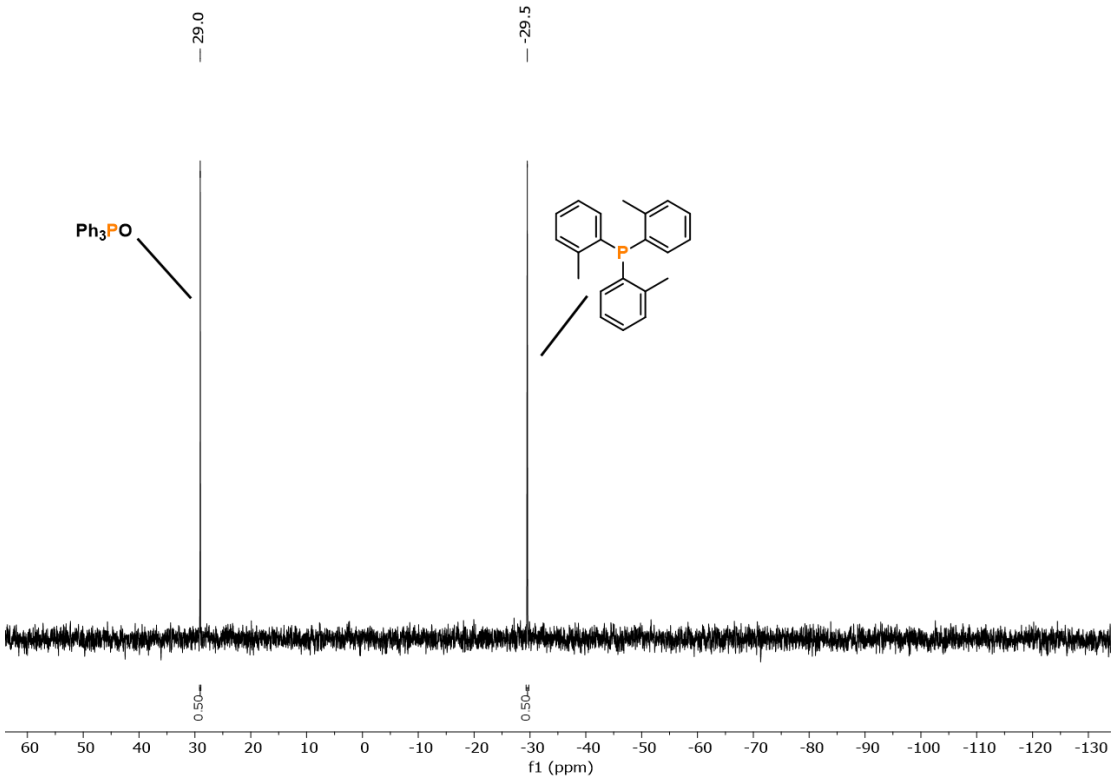


Figure S45. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 2-bromotoluene after 44 h reaction time.

S4.2.5 Tetra(*m*-tolyl)phosphonium bromide and tris(*m*-tolyl)phosphine

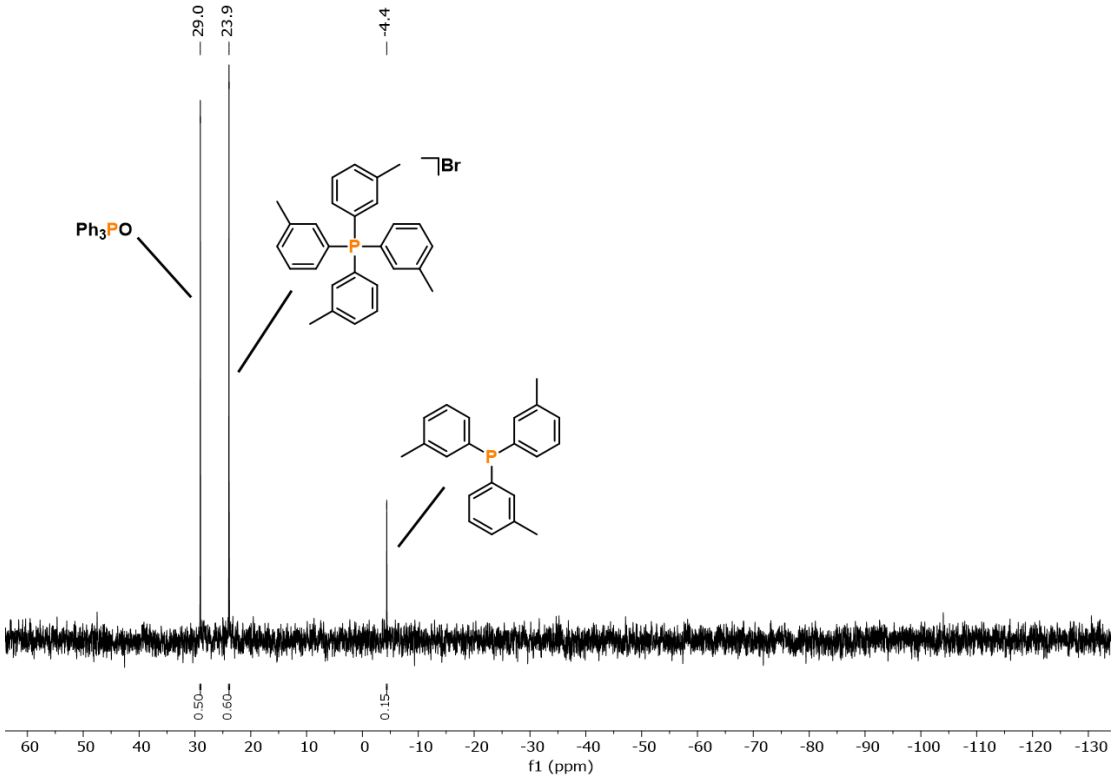


Figure S46. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-bromotoluene after 44 h reaction time.

S4.2.6 Tetrakis(3-ethylphenyl)phosphonium bromide and tris(3-ethylphenyl)phosphine[5]

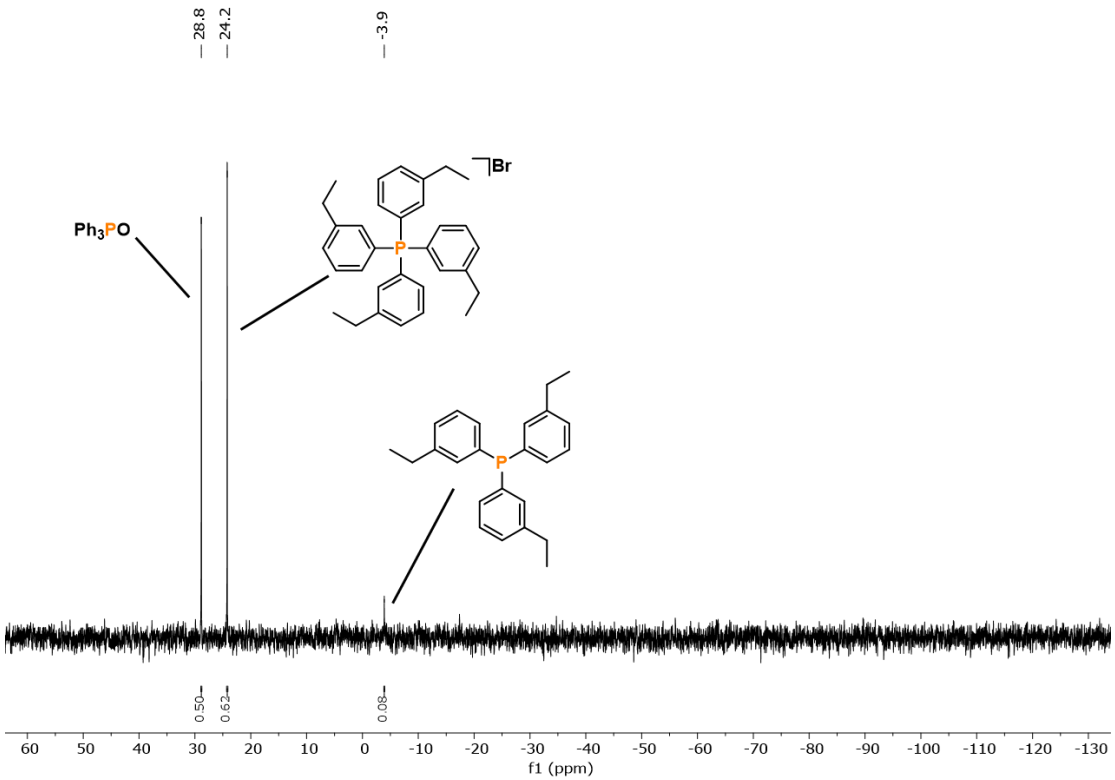


Figure S47. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-bromo-3-ethylbenzene after 44 h reaction time.

S4.2.7 Tetrakis[(4-*tert*-butyl)phenyl]phosphonium bromide and tris[(4-*tert*-butyl)phenyl]phosphine

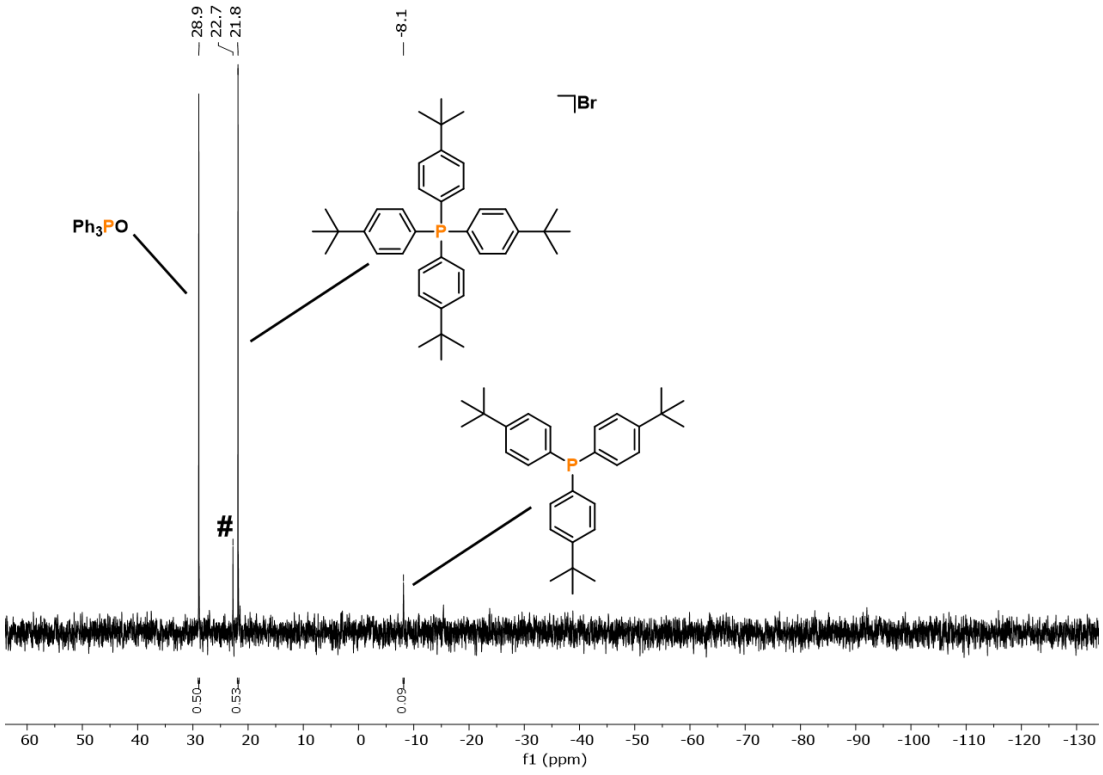


Figure S48. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-bromo-*tert*-butylbenzene after 44 h reaction time. #: unidentified signal.

S4.2.8 Tetrakis[(4-trifluoromethyl)phenyl]phosphonium bromide and tris[(4-trifluoromethyl)phenyl]-phosphine

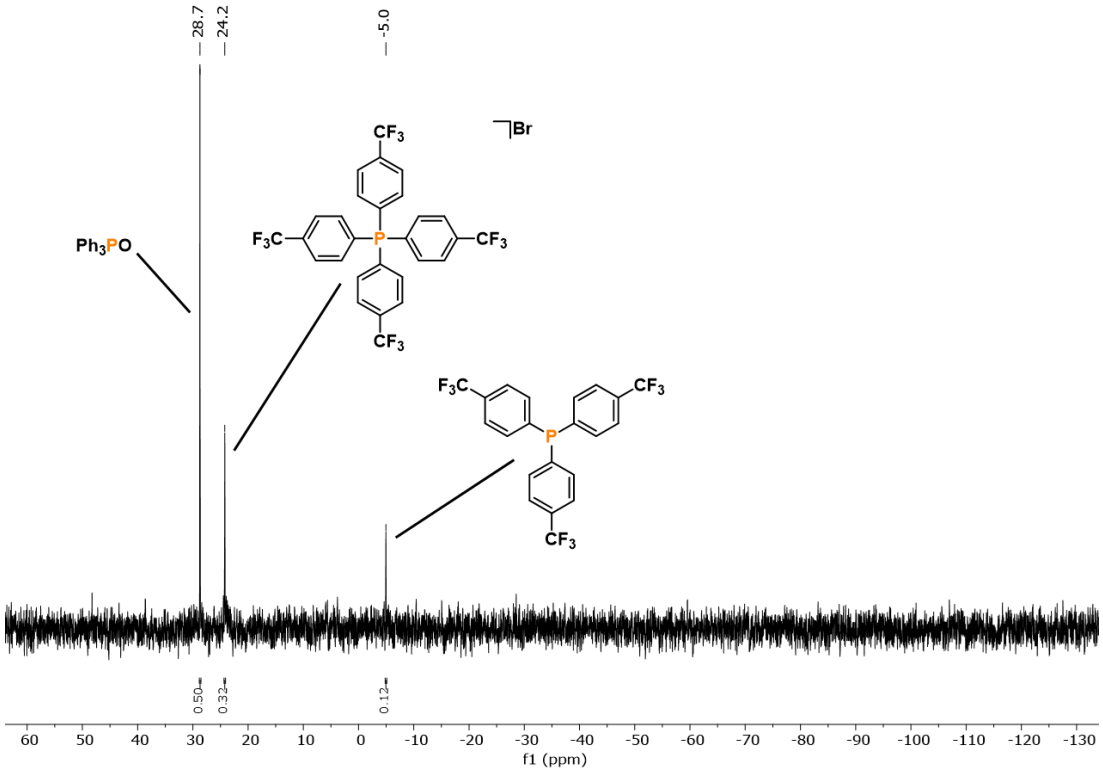


Figure S49. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-bromobenzotrifluoride after 44 h reaction time.

S4.2.9 Tetrakis(4-methyl benzoate)phosphonium bromide and tris(4-methyl benzoate)phosphine

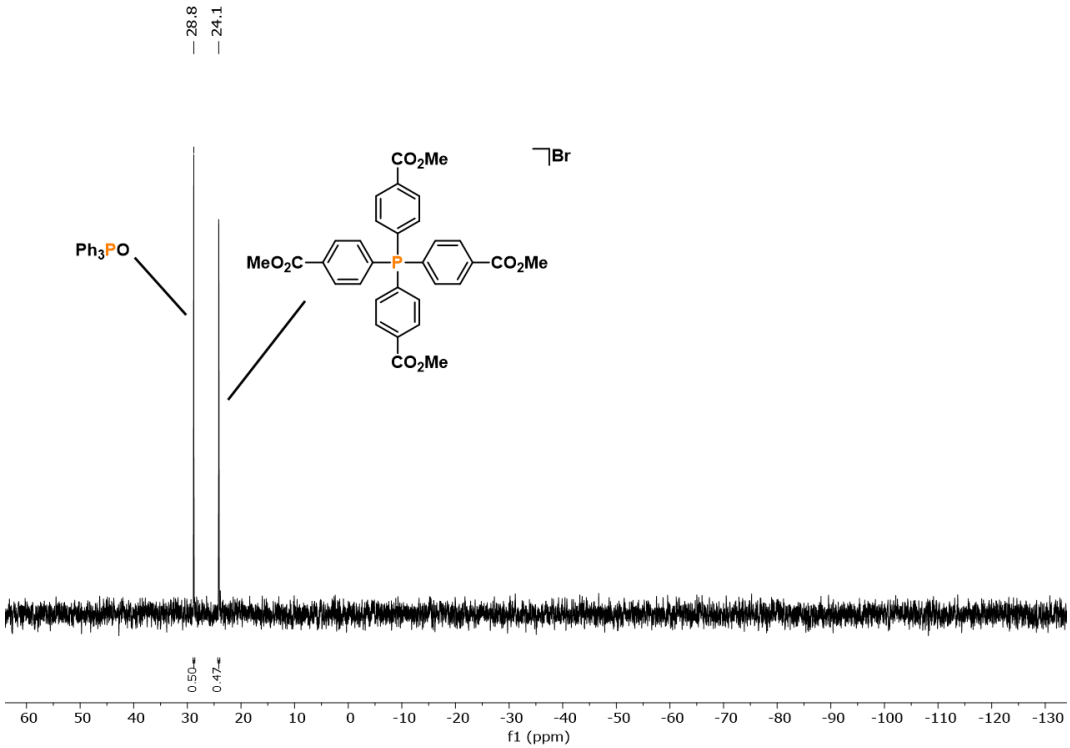


Figure S50. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using methyl 4-bromobenzoate after 44 h reaction time.

Aryl chlorides – 68 h reaction time:

S4.2.10 Tetrakis(3-methoxyphenyl)phosphonium chloride and tris(3-methoxyphenyl)phosphine

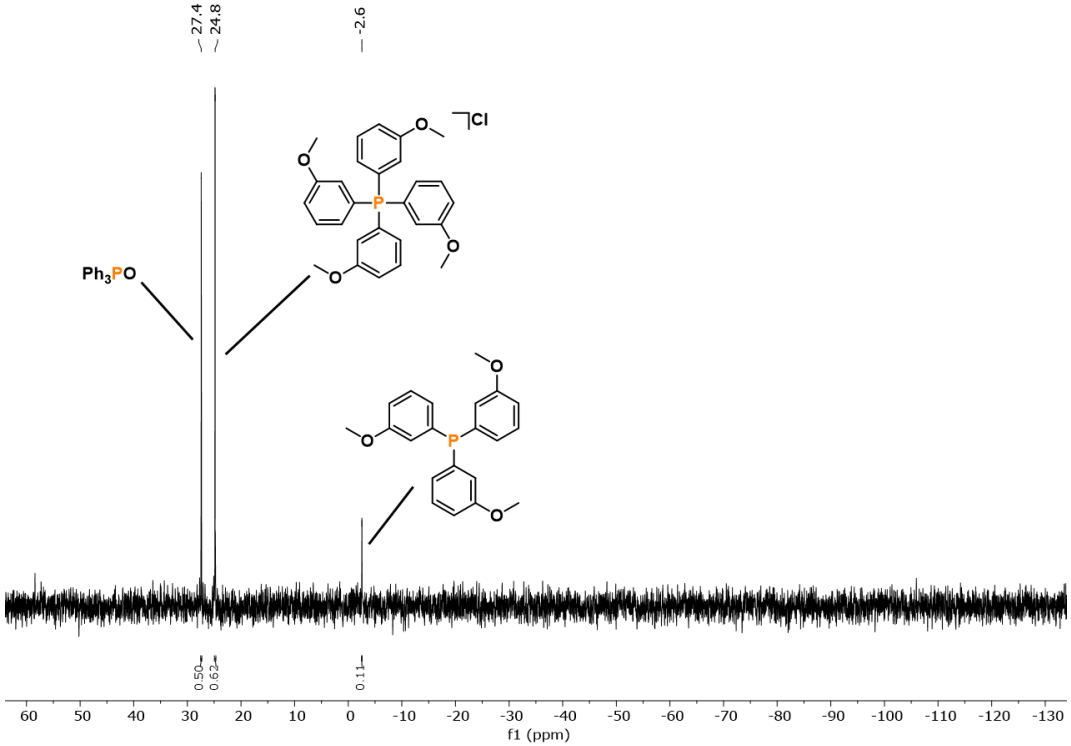


Figure S51. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 3-chloroanisole after 68 h reaction time.

S4.2.11 Tris(*o*-tolyl)phosphine

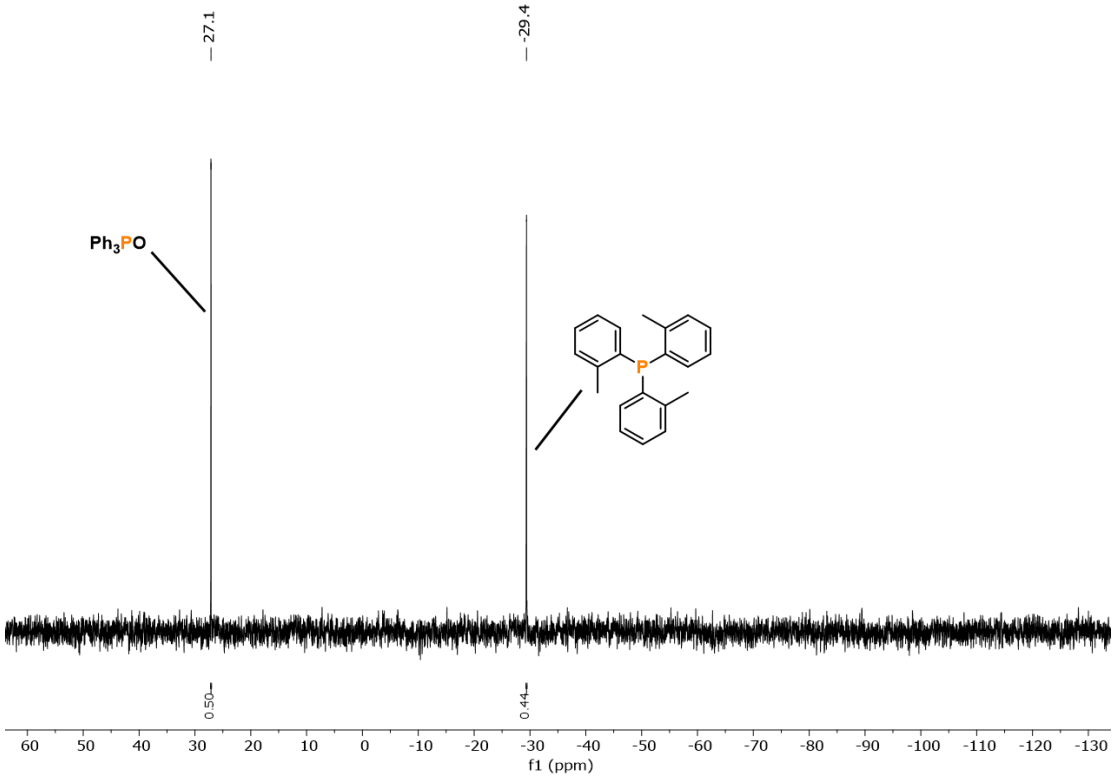


Figure S52. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 2-chlorotoluene after 68 h reaction time.

S4.2.12 Tetrakis(3-ethylphenyl)phosphonium chloride and tris(3-ethylphenyl)phosphine[5]

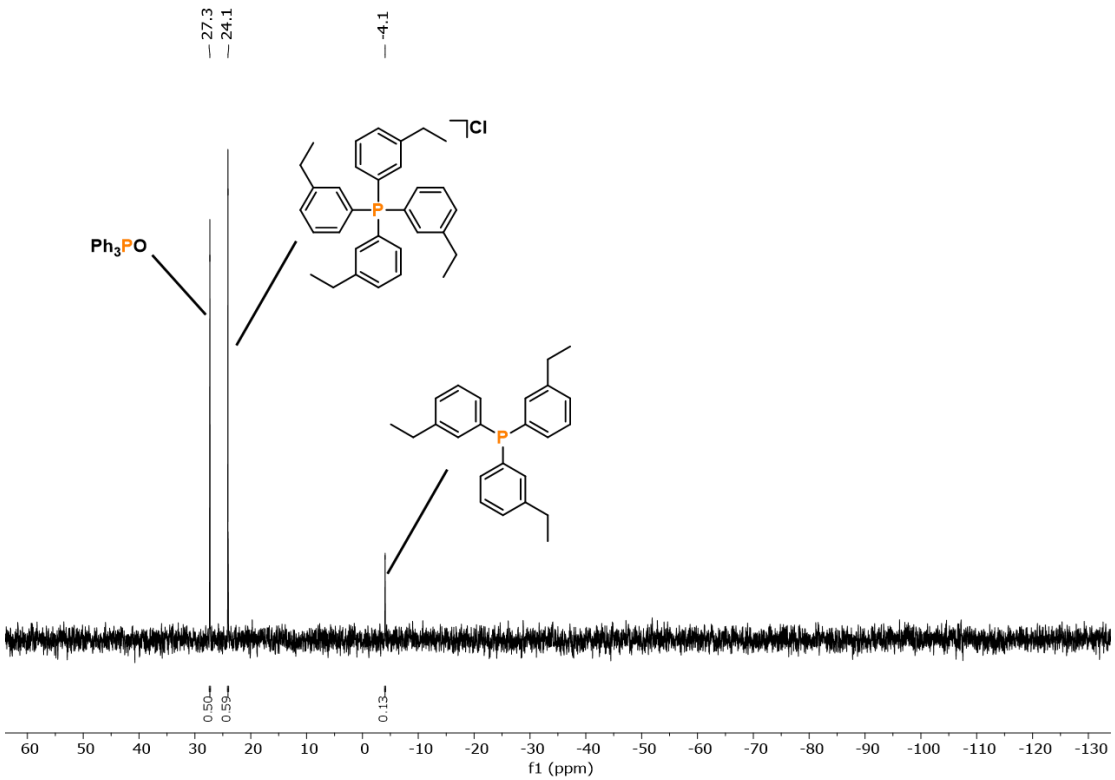


Figure S53. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 1-chloro-3-ethylbenzene after 68 h reaction time.

S4.2.13 Tris[(4-trifluoromethyl)phenyl]phosphine

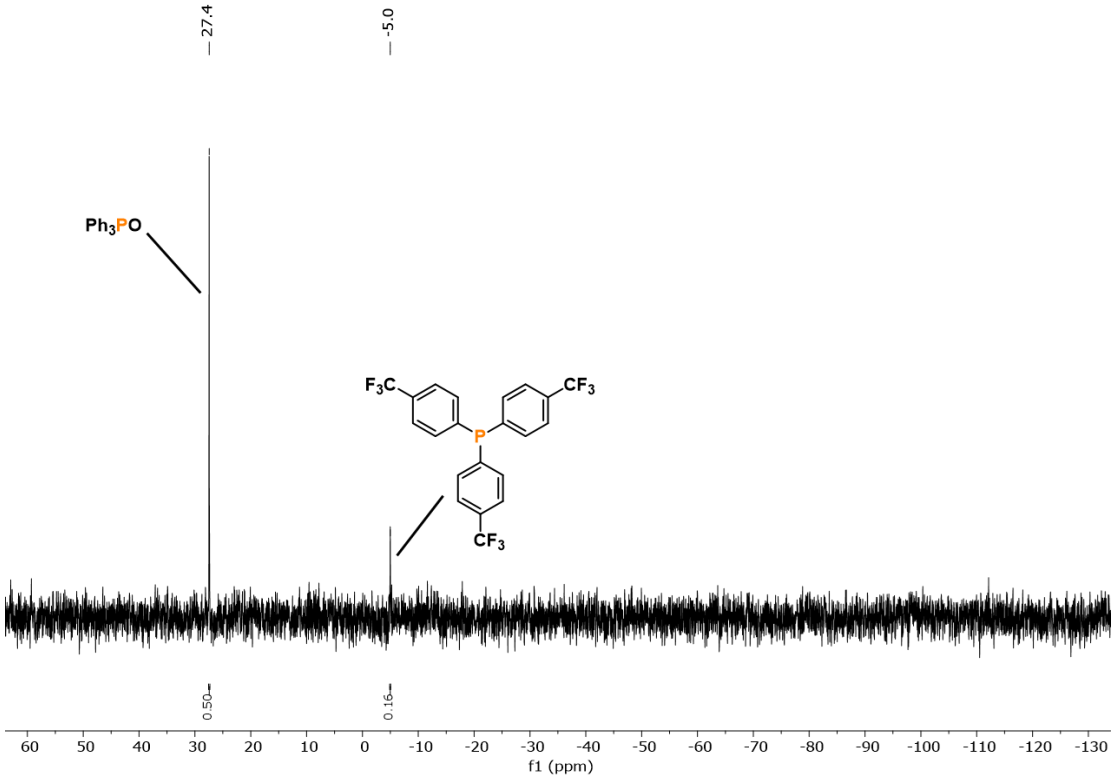


Figure S54. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using 4-chlorobenzotrifluoride after 68 h reaction time.

S4.2.14 Tris(4-methyl benzoate)phosphine

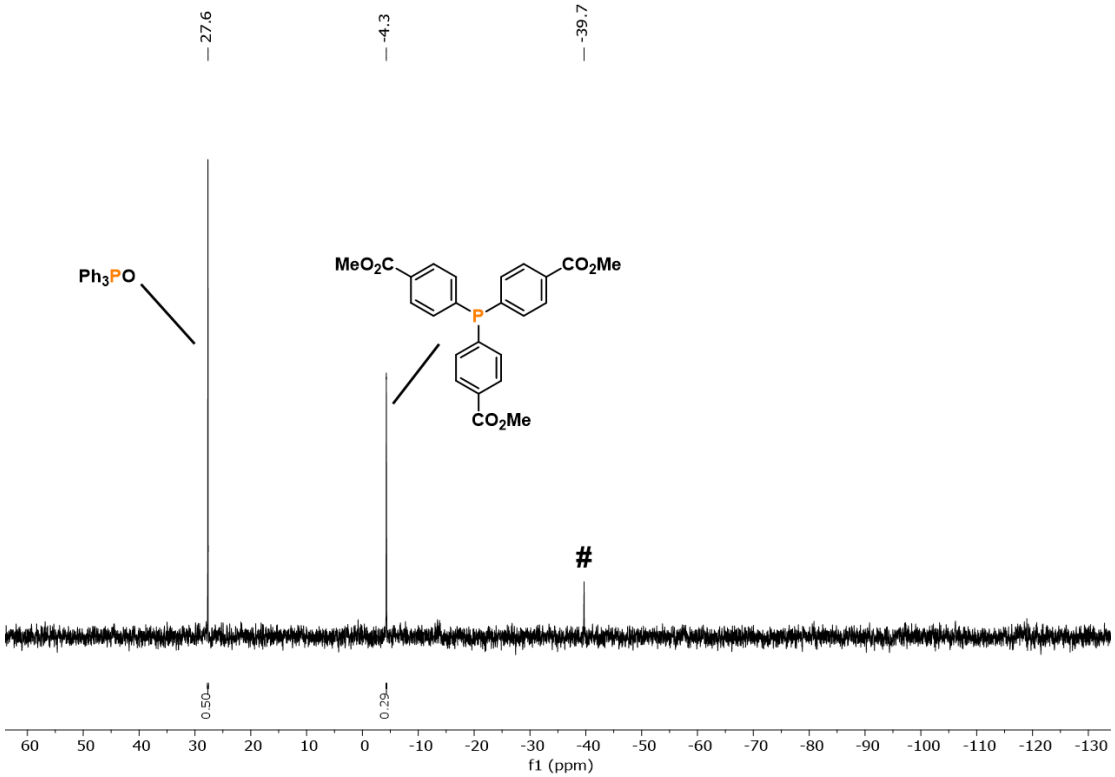
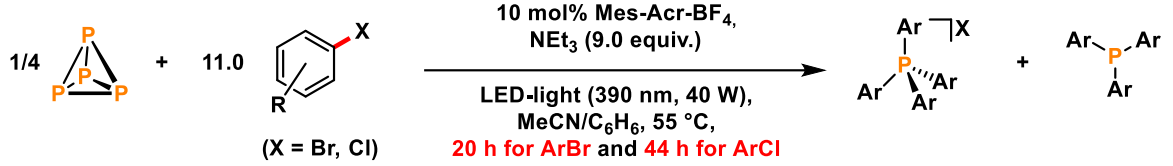
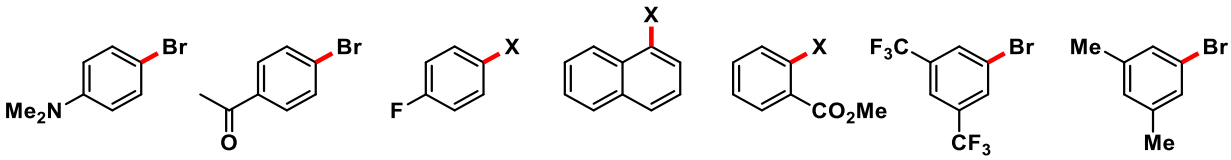


Figure S55. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of P_4 using methyl 4-chlorobenzoate after 68 h reaction time. #: Ar_2PH; Ar = 4-methylcarboxyphenyl.

S4.3. Reaction data for additional and unsuccessful substrates (X = Br, Cl)

Table S12. Photocatalytic functionalization of P_4 to $[Ar_4P]X$ (X = Br, Cl) and Ar_3P: Additional and unsuccessful substrates.[a]





Entry	Substrate		Full conv. of P_4?	Form. of $[Ar_4P]X$ / %	Form. of Ar_3P / %
	X	R			
1	Br	R = 4-NMe_2	✓	0	0
2	Br	R = 4-C(O)Me	✓	0	0
3	Br	R = 4-F	✓	25[b]	10
4	Cl	R = 4-F	✓	0	10
5	Br	R = 1-Napht.	✓	0	24
6	Cl	R = 1-Napht.	✓	0	7
7	Br	R = 2-CO_2Me	✓	0	0
8	Cl	R = 2-CO_2Me	✓	0	4
9	Br	3,5-$(CF_3)_2$	✓	0	9
10	Br	3,5-Me_2	✓	14	28

[a] For the general procedure, see section S2. [b] Additional unidentified signal with a similar chemical shift as the phosphonium salt signal.

S5. Synthesis of $[Ph_4P]Br$ and $(o\text{-tol})_3P$ on a preparative scale

Tetraphenylphosphonium bromide, $[Ph_4P]Br$:

To a 100 mL stoppered Schlenk tube equipped with a stirring bar were added bromobenzene (926.7 µL, 8.8 mmol, 11.0 equiv. based on the phosphorus atom), NEt_3 (1004 µL, 7.2 mmol, 9.0 equiv. based on the phosphorus atom), 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (Mes-Acr-BF_4; 45.9 mg, 0.08 mmol, 10 mol% based on the phosphorus atom) and P_4 (24.8 mg, 0.2 mmol, 0.25 equiv., as a stock solution in 1306 µL benzene). The mixture was dissolved in acetonitrile (2.0 mL). The tube was sealed, fixed with a clamp (Figure S56), and irradiated with nUV light (390 nm, 40 W, Kessil PR160L in a PR160 Rig with Fan Kit) for 48 h. Ph_3PO (0.4 mmol, 111.2 mg; added as solid) was subsequently added to act as an internal standard. The resulting mixture was subjected to quantitative $^{31}P\{^1H\}$ NMR analysis, which showed formation of 66% tetraphenylphosphonium bromide and 2% triphenylphosphine (Figure S57).

Figure S56. Setup used for photocatalytic reactions at 0.8 mmol scale of P_4.

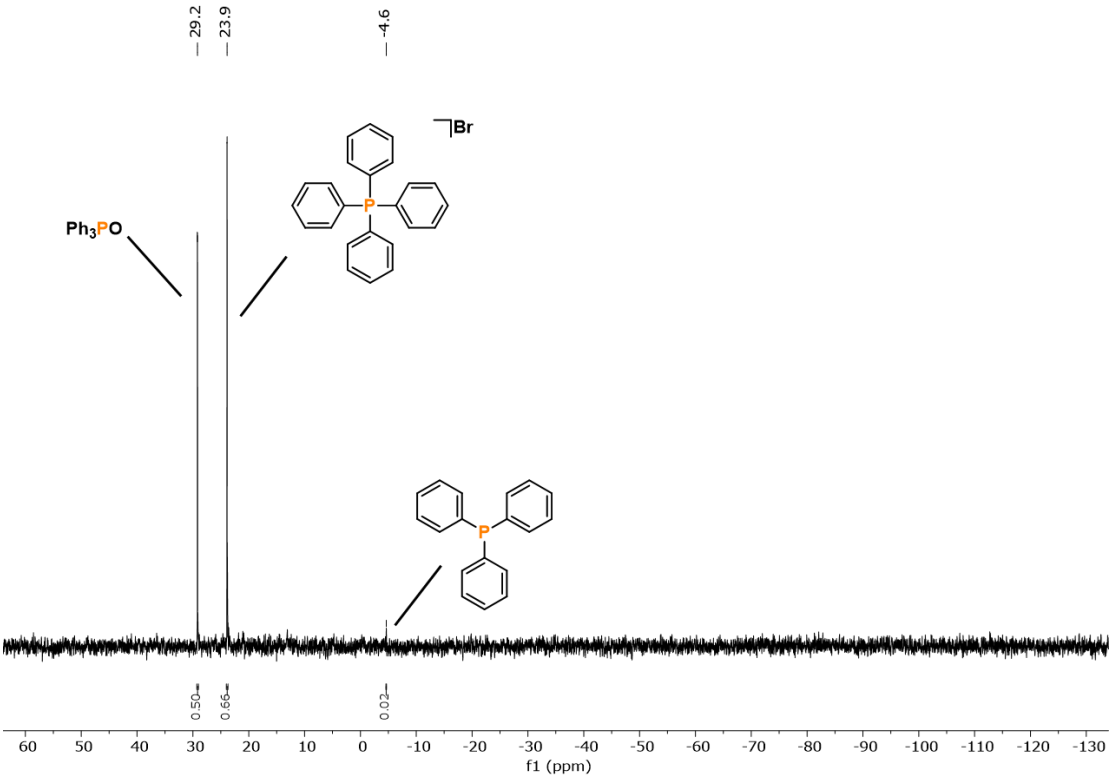


Figure S57. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the 20-fold scale-up photocatalytic functionalization of P_4 using bromobenzene.

Work-up (without addition of internal standard Ph_3PO):

The suspension was evaporated to dryness in vacuo at 100 °C, and the resulting orange wax-like residue was dispensed in Et_2O (2 x 20 mL), manually scratched, sonicated for 30 min, and filtered to give a pale yellow solid. The solid was dried again *in vacuo*, dissolved in CH_2Cl_2 (10 mL) and extracted with aqueous HBr (3 x 20 mL; 1 mL HBr 47%wt in 50 mL H_2O, pH = 1) to remove NEt_3·HBr. The combined aqueous phases were re-extracted with CH_2Cl_2 (1 x 10 mL). The combined organic phase was added to H_2O (300 mL). The emulsion was concentrated to ca. 200 mL using a rotary evaporator at 50 °C, after which the separation of an orange wax-like precipitate was observed (precipitation of an orange waxy solid at glass wall was already observed during the extraction step). The concentrated solution was filtered (Sartorius, filter paper grade 1289), and the clear pale-yellow filtrate was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (10 mL) and the resulting pale-yellow solution was added dropwise to a solution of Et_2O (100 mL) while stirring. An off-white solid precipitated, which was isolated by filtration and dried under reduced pressure. The obtained solid was dissolved in CH_2Cl_2 (30 mL) and charcoal (3.0 g) was added to the solution. The suspension was stirred for 30 min at ambient temperature and filtered (sartorius, filter paper grade 1289) to obtain a clear, pale-yellow filtrate. The solvent was removed *in vacuo*. Recrystallization of the solid residue from CH_2Cl_2/Et_2O (1:3, 5:15 mL) yielded an off-white, NMR-spectroscopically clean solid, which was dried at 100 °C under reduced pressure for 1 day (130.1 mg, 39%). The NMR spectroscopic data are consistent with the data reported in the literature.[10]

^{1}H NMR (400.13 MHz, $CDCl_3$, 300 K): δ = 7.95-7.86 (m, 1H), 7.83-7.73 (m, 2H), 7.68-7.57 (m, 2H).

^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$, 300 K): δ = 136.0 (d, *J* = 3.1 Hz), 134.6 (d, *J* = 10.2 Hz), 131.0 (d, *J* = 12.9 Hz), 117.6 (d, *J* = 89.4 Hz).

^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$, 300 K): δ = 23.8 (s).

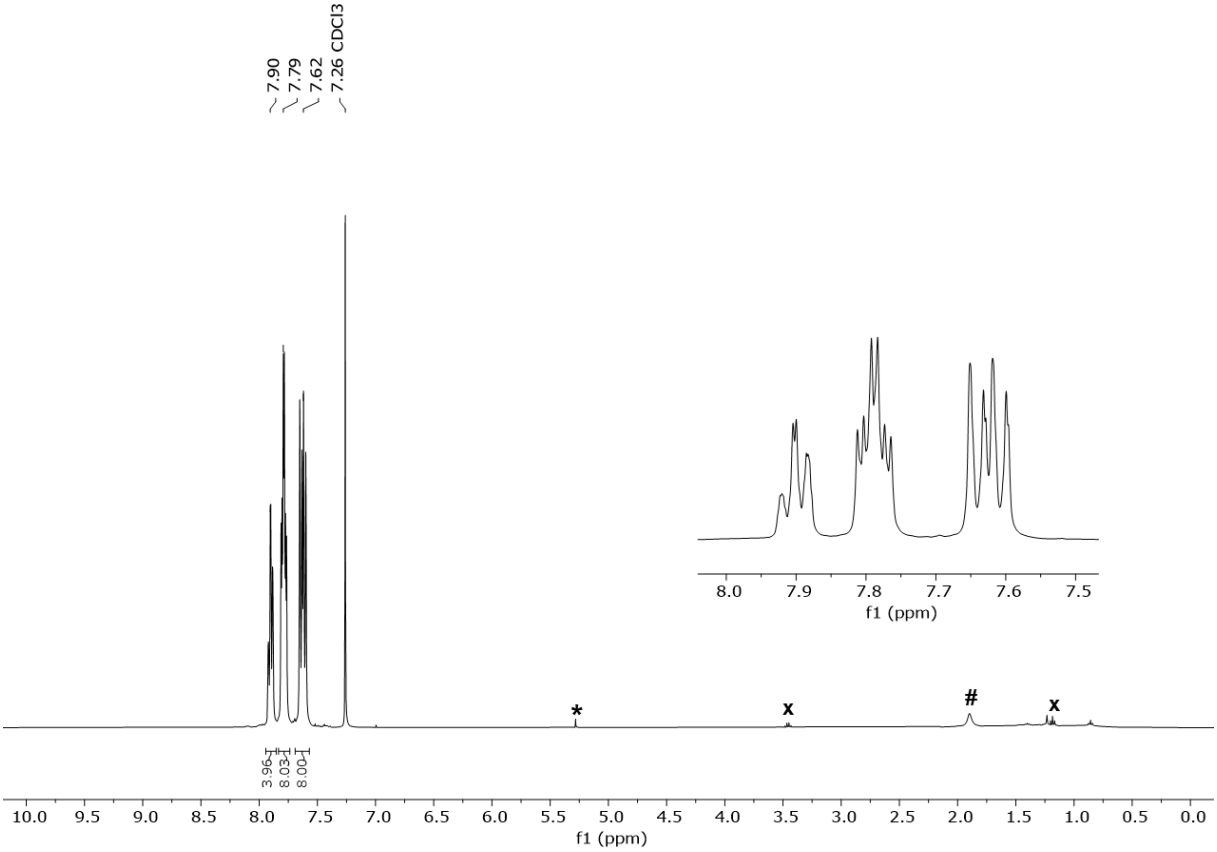


Figure S58. ^{1}H NMR spectrum (400.13 MHz, $CDCl_3$, 300 K) of tetraphenylphosphonium bromide prepared from P_4 on a 0.8 mmol scale. *: residual CH_2Cl_2; x: residual Et_2O; #: residual water from $CDCl_3$.

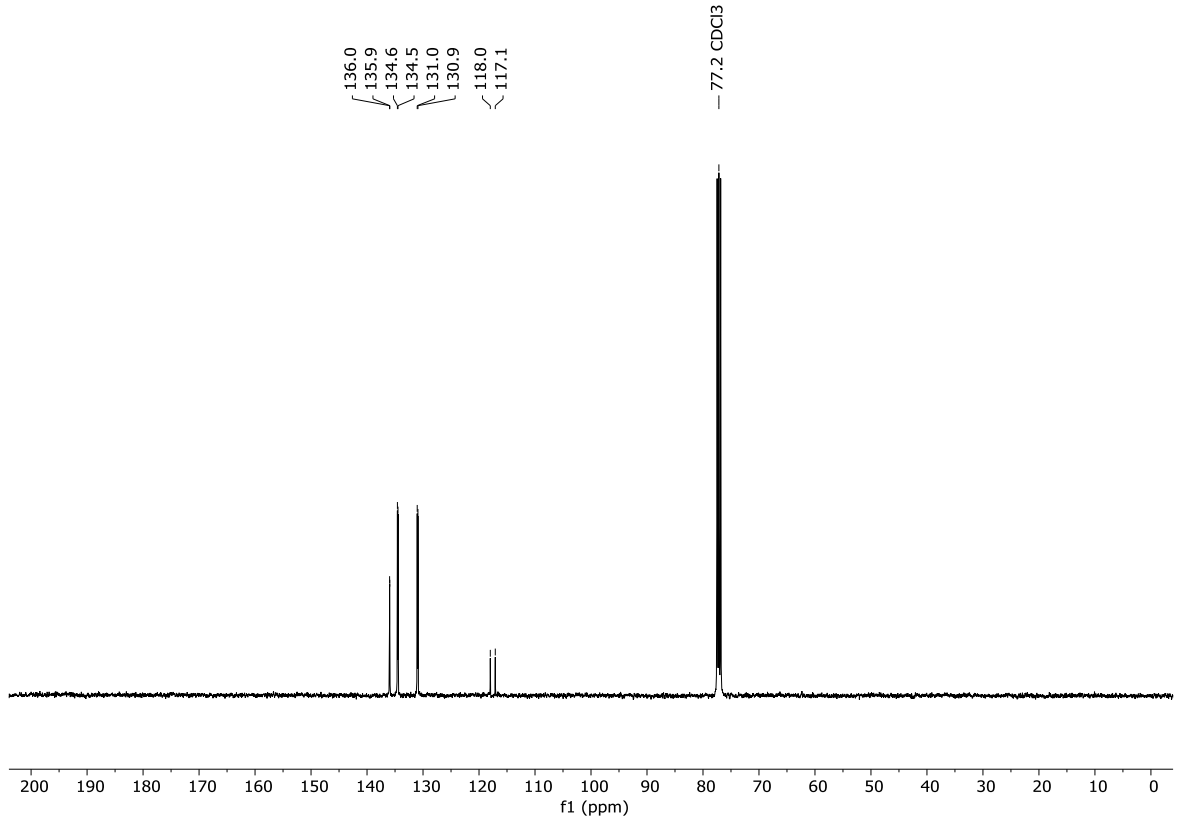


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, $CDCl_3$, 300 K) of tetraphenylphosphonium bromide prepared from P_4 on a 0.8 mmol scale.

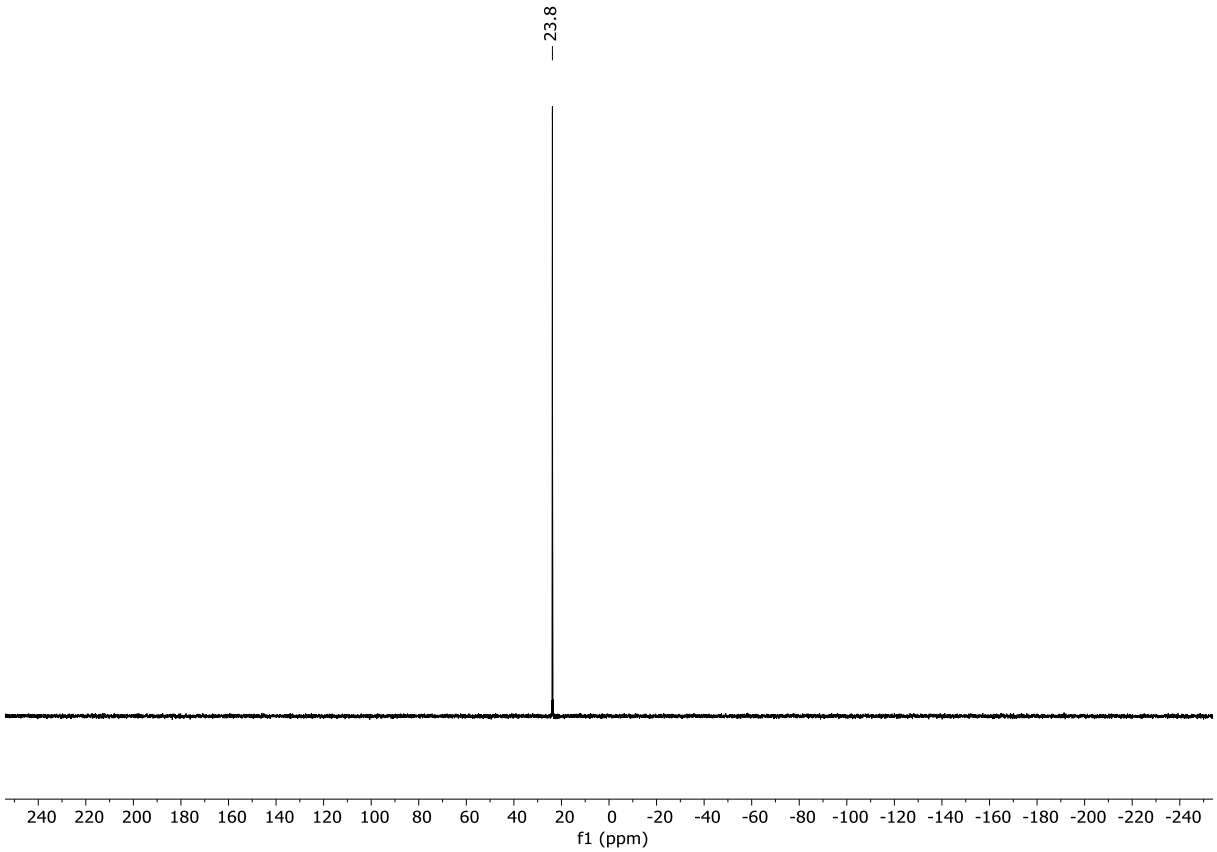


Figure S60. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, $CDCl_3$, 300 K) of tetraphenylphosphonium bromide prepared from P_4 on a 0.8 mmol scale.

Tris(o-tolyl)phosphine, (o-tol)$_3$P:

To a 100 mL stoppered Schlenk tube equipped with a stirring bar were added 2-bromotoluene (1058 µL, 8.8 mmol, 11.0 equiv. based on the phosphorus atom), NEt_3 (1004 µL, 7.2 mmol, 9.0 equiv. based on the phosphorus atom), 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (Mes-Acr-BF_4; 45.9 mg, 0.08 mmol, 10 mol% based on the phosphorus atom) and P_4 (24.8 mg, 0.2 mmol, 0.25 equiv., as a stock solution in 1306 µL benzene). The mixture was dissolved in acetonitrile (2.0 mL). The tube was sealed, fixed with a clamp (Figure S56), and irradiated with nUV light (390 nm, 40 W, Kessil PR160L in a PR160 Rig with Fan Kit) for 48 h. Ph_3PO (0.4 mmol, 111.2 mg; added as solid) was subsequently added to act as an internal standard. The resulting mixture was subjected to quantitative $^{31}P\{^1H\}$ NMR analysis and showed formation of 42% tris(*o*-tolyl)phosphine and minor formation of di(*o*-tolyl)phosphine (Figure S61).

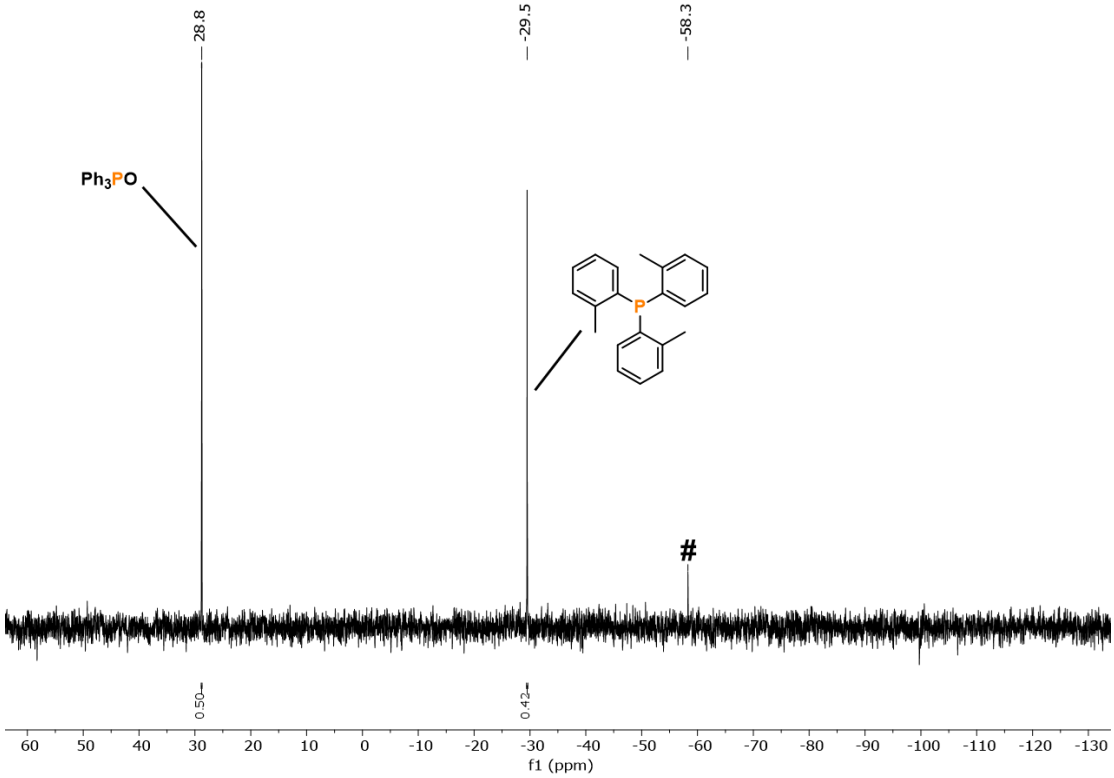


Figure S61. Quantitative single scan $^{31}P\{^1H\}$ (zgig) NMR spectrum for the 20-fold scale-up photocatalytic functionalization of P_4 using 2-bromotoluene. #: di(*o*-tolyl)phosphine.

Work-up (without addition of internal standard Ph_3PO):

The suspension was evaporated to dryness in vacuo at 100 °C, and the resulting orange wax-like residue was treated with *n*-hexane (30 mL). The mixture was stirred for 2 h, and the clear, pale-yellow supernatant filtered into a sublimation flask. The solvent was removed *in vacuo* and the residual orange wax-like solid was sublimed twice (ca. 1.0×10^{-2} mbar to ca. 6.0×10^{-3} mbar, 100 °C) to give an off-white solid (67 mg, 28%). The NMR spectroscopic data are consistent with the data reported in the literature.[11]

^{1}H NMR (400.13 MHz, $CDCl_3$, 300 K): δ = 7.29-7.20 (m, 6H), 7.10-7.03 (m, 3H), 6.76-6.67 (m, 3H), 2.39 (s, 9H).

^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$, 300 K): δ = 142.9 (d, *J* = 26.1 Hz), 134.7 (d, *J* = 11.0 Hz), 133.2 (s), 130.2 (d, *J* = 4.8 Hz), 128.8 (s), 126.3 (s), 21.3 (d, *J* = 21.4 Hz).

^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$, 300 K): δ = –28.9 (s).

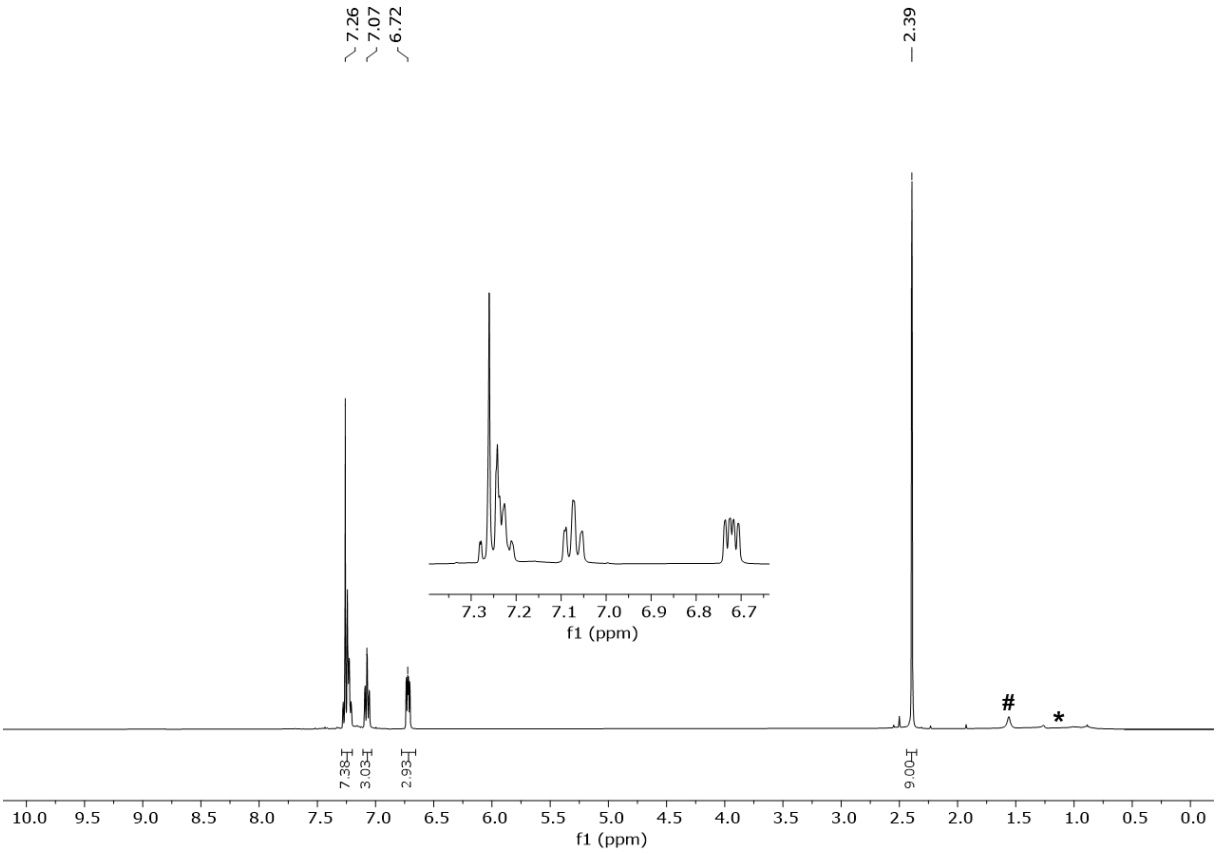


Figure S62. ^{1}H NMR spectrum (400.13 MHz, $CDCl_3$, 300 K) of tris(*o*-tolyl)phosphine prepared from P_4 on a 0.8 mmol scale. #: residual water from $CDCl_3$; *: residual *n*-hexane.

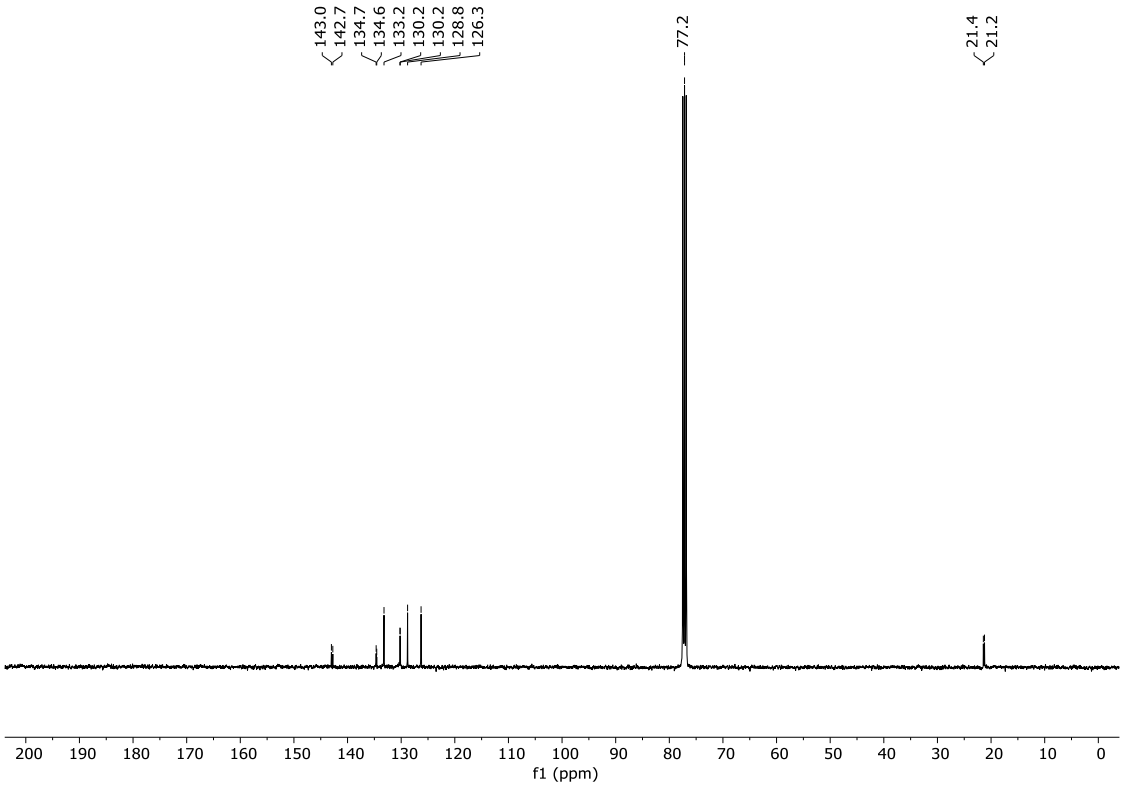


Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, $CDCl_3$, 300 K) of tris(*o*-tolyl)phosphine prepared from P_4 on a 0.8 mmol scale.

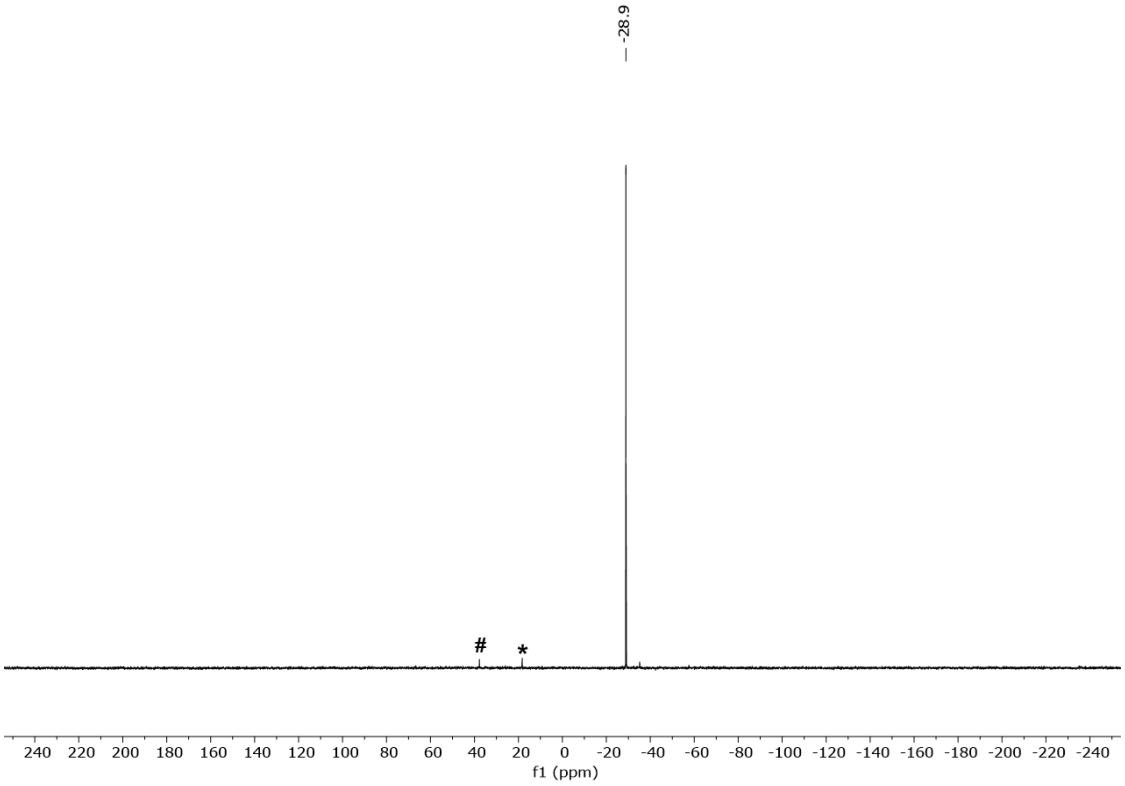


Figure S64. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, $CDCl_3$, 300 K) of tris(*o*-tolyl)phosphine prepared from P_4 on a 0.8 mmol scale. #: tris(*o*-tolyl)phosphine oxide. *: bis(*o*-tolyl)phosphine oxide.

S6. NMR spectroscopic investigations

Reaction monitoring and intermediate identification:

The reaction mixture was prepared according to the general procedure (see section S2) using bromobenzene as the substrate. The individual reactions were stopped after the indicated reaction time (see Table S10), internal standard (Ph_3PO; 0.02 mmol, stock solution in benzene) was added, and the mixture subjected to quantitative $^{31}P\{^1H\}$ NMR analysis. The NMR spectroscopic reaction monitoring is depicted in Figure S65. In the $^{31}P\{^1H\}$ NMR spectrum (NS 512) after 1 h reaction time, the formation of mono- and diphosphorus intermediates can be observed (Figure S66).

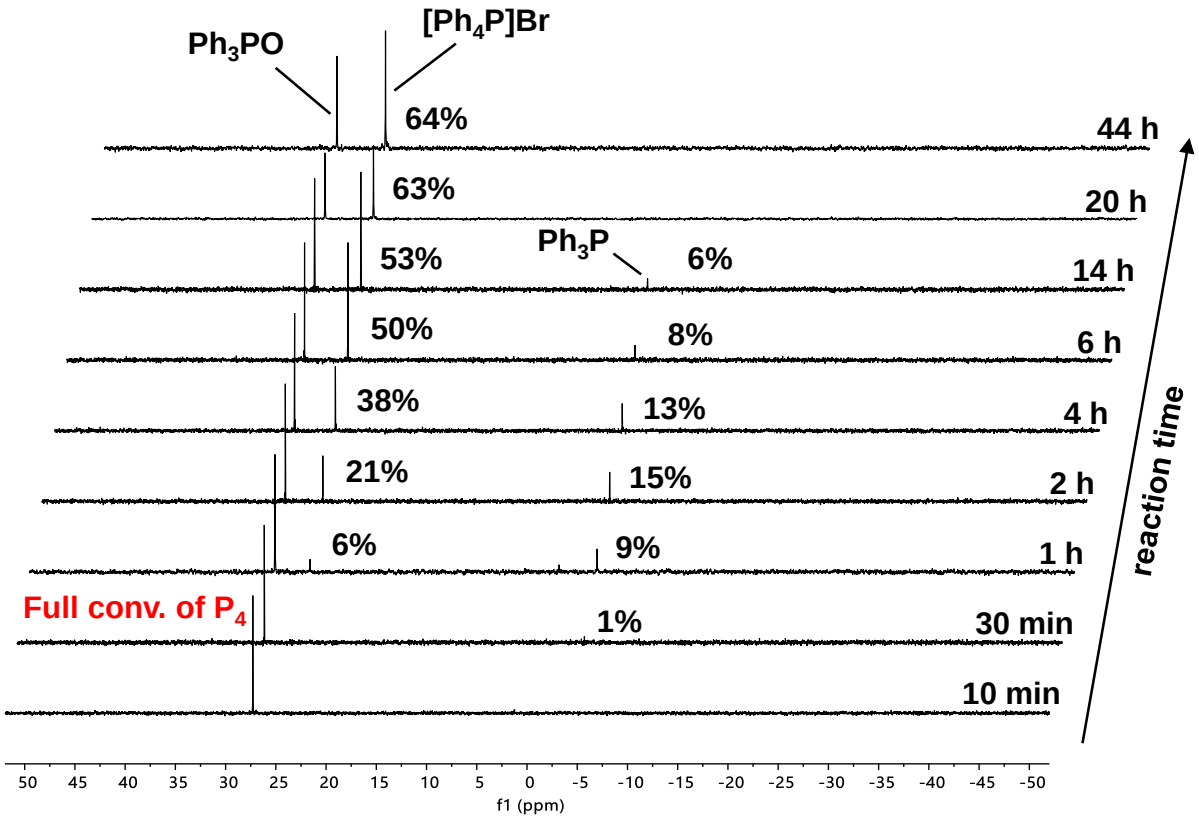


Figure S65. $^{31}P\{^1H\}$ NMR spectroscopic reaction monitoring (t ≤ 44 h) of the photocatalytic phenylation of P_4 using standard conditions (see section S2).

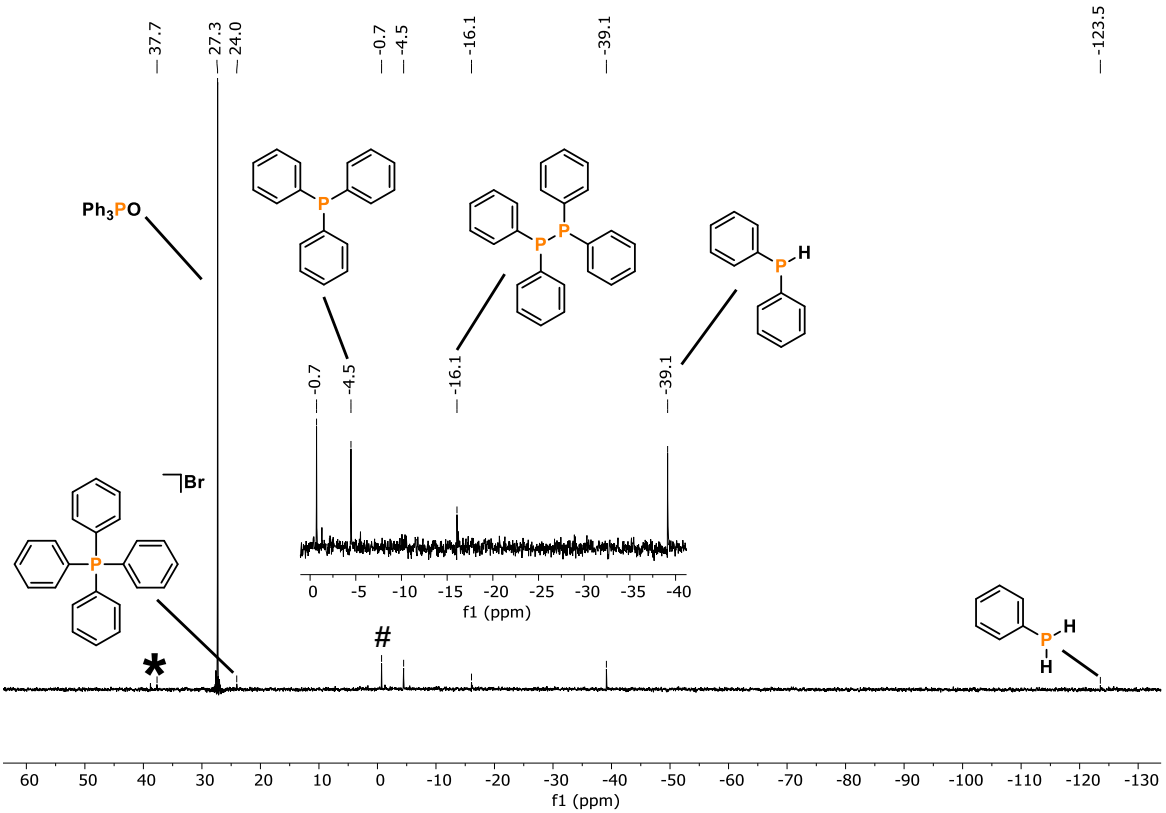


Figure S66. $^{31}P\{^{1}H\}$ NMR spectroscopic reaction monitoring (t ≤ 44 h) of the photocatalytic phenylation of P_4 using standard conditions (see section S2). $^{31}P\{^{1}H\}$ NMR spectrum (NS 512) after 1 h reaction time. #: unidentified signal. *: Formation of $[Ph_2P(NEt_2)(CH{=}CHCH{=}CHNEt_2)]Br$ (37.7 ppm).[1]

Assessment of PH_3 formation and identification of additional reaction intermediates:

A) The reaction mixture was prepared according to the general procedure (see section S2), but in absence of aryl substrate and on a threefold scale up. The reaction mixture was transferred into a J. Young NMR tube and irradiated with nUV light (390 nm, 40 W, Kessil PR160L in a PR160 Rig with Fan Kit, Figure S2, right) for 20 h. After that, the mixture was subjected to $^{31}P\{^{1}H\}$ NMR analysis. In the $^{31}P\{^{1}H\}$ NMR spectrum (NS 20480), a major signal for residual P_4 at –523.1 ppm can be observed. Next to this, a series of unidentified signals residing between 4.0 and –8.0 ppm can be observed. The formation of PH_3 only appears in a negligible amount as indicated by the quartet signal at –241.4 ppm, which can only be observed with adequate resolution after 20480 scans. Thus, in the absence of aryl substrate, P–H bond formation ultimately resulting in PH_3 does not seem to be a significant process.

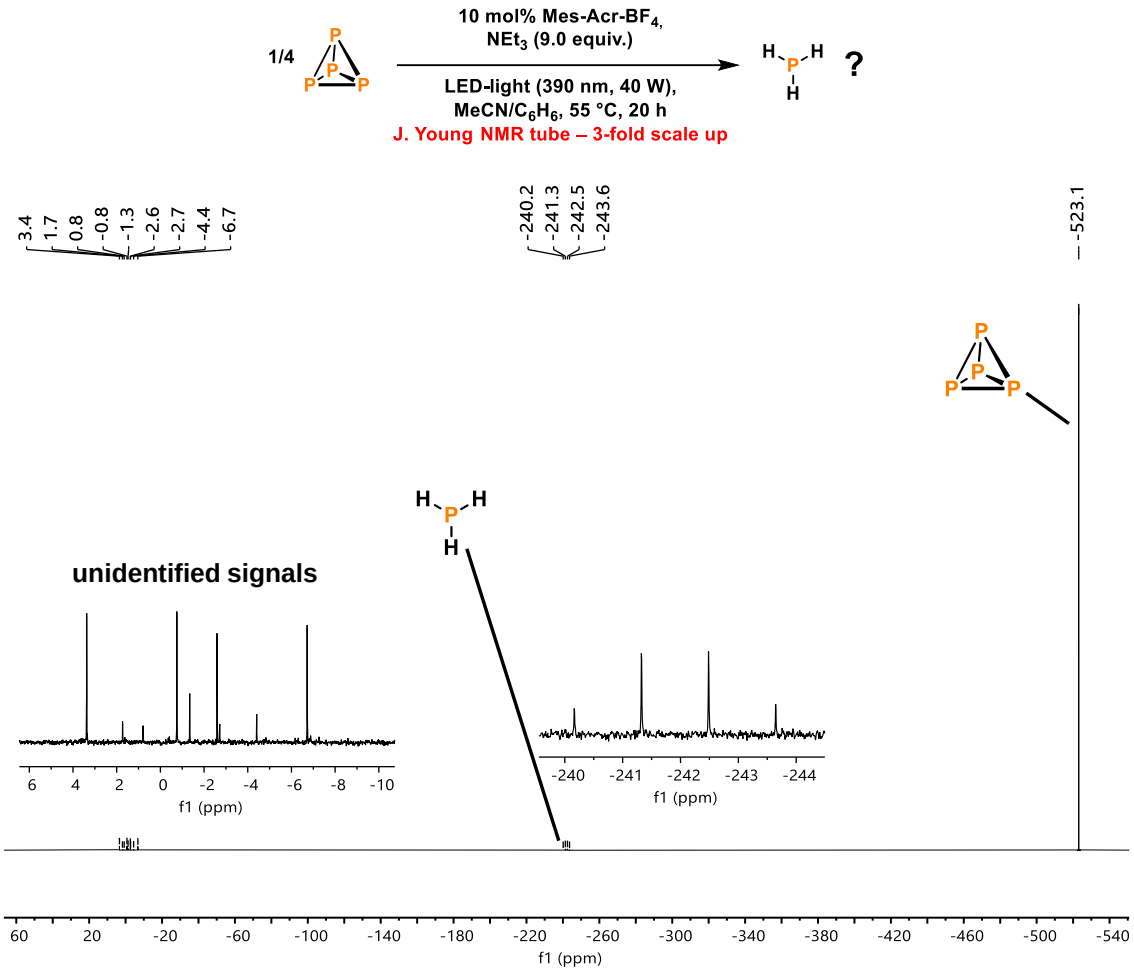


Figure S67. ^{31}P NMR spectrum (161.98 MHz, C_6D_6, 300 K, NS 20480) of the attempted PH_3 formation using photocatalytic conditions in the absence of substrate.

B) The reaction mixture was prepared according to the general procedure (see section S2), with bromobenzene as the aryl substrate and on a threefold scale-up. The reaction mixture was transferred into a J. Young NMR tube and irradiated with nUV light (390 nm, 40 W, Kessil PR160L in a PR160 Rig with Fan Kit, Figure S2, right) for 20 h (formation of 53% $[Ph_4P]Br$ and 3% Ph_3P). The mixture was subjected to $^{31}P\{^1H\}$ NMR analysis after 20 min, 1 h, 3 h, 9 h and 20 h. The progress of product formation was assessed with a standard capillary bearing Ph_3PO (0.02 mmol in MeCN-d_3). The NMR spectroscopic reaction monitoring is depicted in Figure S68. During the monitoring, no formation of PH_3 was observed at any time (Figure S68, see absence of signal between –236 and –250 ppm). In addition, while not all P_4 was consumed after 3 h irradiation, the formation of $PhPH_2$ and Ph_2PH next to other monophosphorus intermediates (Figure S68, see a-f) could be observed.[1] This is a strong indication, that the breakdown of P_4 does not primarily result in the formation of PH_3 but likely proceeds through other intermediates, e.g. linear or cyclic polyphosphorus species, "P_nR_x" with n = 2-4, which could not be identified (apart from the diphosphine Ph_4P_2 and the divinyldiphosphine $[PhP(CHCH_2)]_2$). Accordingly, the arylation of $NaPH_2$ as a PH_3-surrogate (*vide infra*) did not furnish

comparable results to the P_4 system based on the use of Mes-Acr-BF_4 as a photocatalyst (*vide infra*, S8). The aminophosphine intermediates and side products, which are primarily observed at 3 and 9 h reaction time do not appear in significant quantities, however, the sum of all species can account for a substantial portion of the overall arylation reaction and thus may present an additional factor limiting the (quantitative) formation of Ar_3P and $[Ar_4P]X$ (X = Br, Cl).

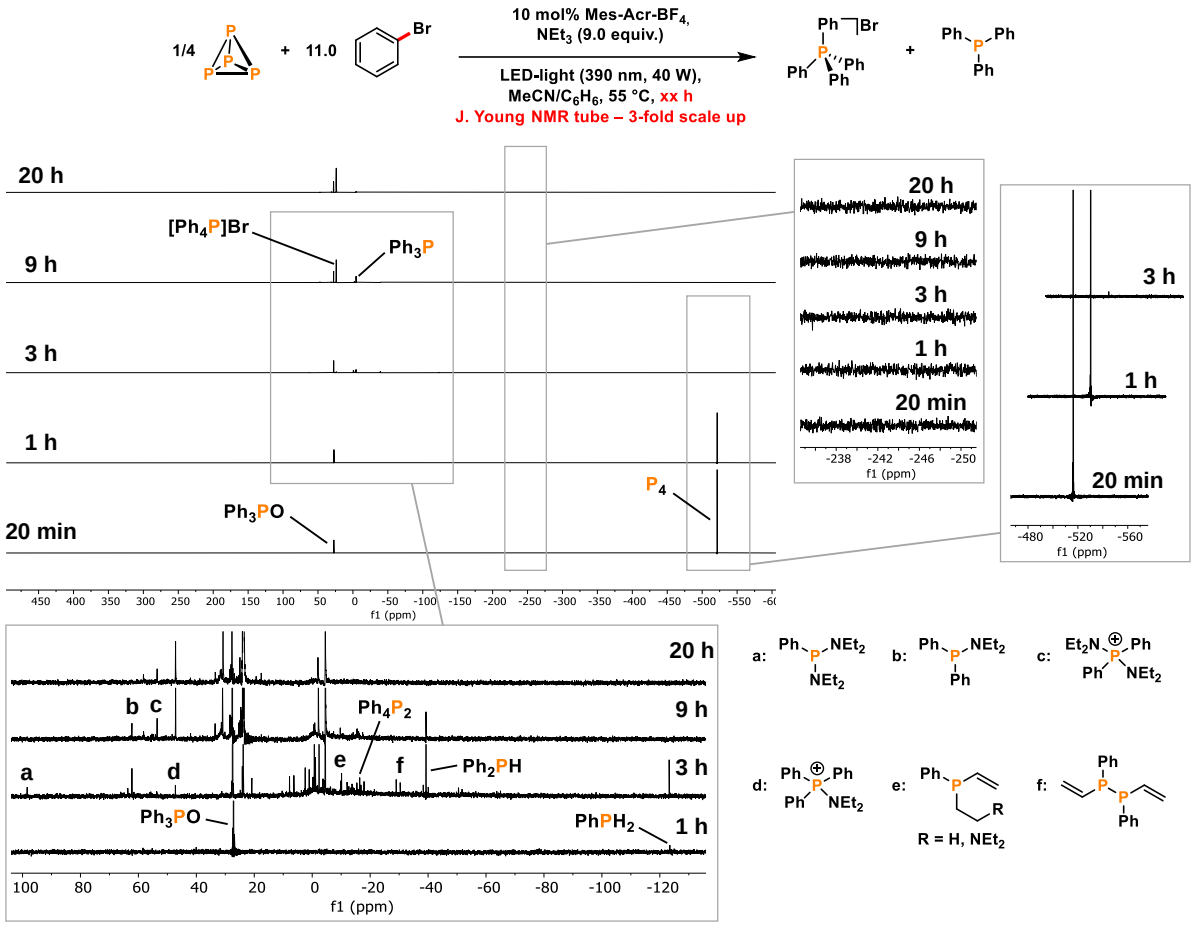


Figure S68. $^{31}P\{^1H\}$ NMR reaction monitoring (161.98 MHz, C_6D_6, 300 K, NS 512) of the phenylation of P_4 in a J. Young NMR tube and identification of additional reaction intermediates and side products in agreement with the literature.[1] No observation of PH_3 formation throughout the whole reaction monitoring.

C) The reaction mixture was prepared according to the general procedure (see section S2), with bromobenzene as the aryl substrate and Ph_5P_5 as P-atom source (instead of P_4) on a threefold scale-up (0.12 mmol P-atom). The reaction mixture was transferred into a J. Young NMR tube and irradiated with nUV light (390 nm, 40 W, Kessil PR160L in a PR160 Rig with Fan Kit, Figure S2, right) for 20 h (formation of 62% $[Ph_4P]Br$, Figure S69).

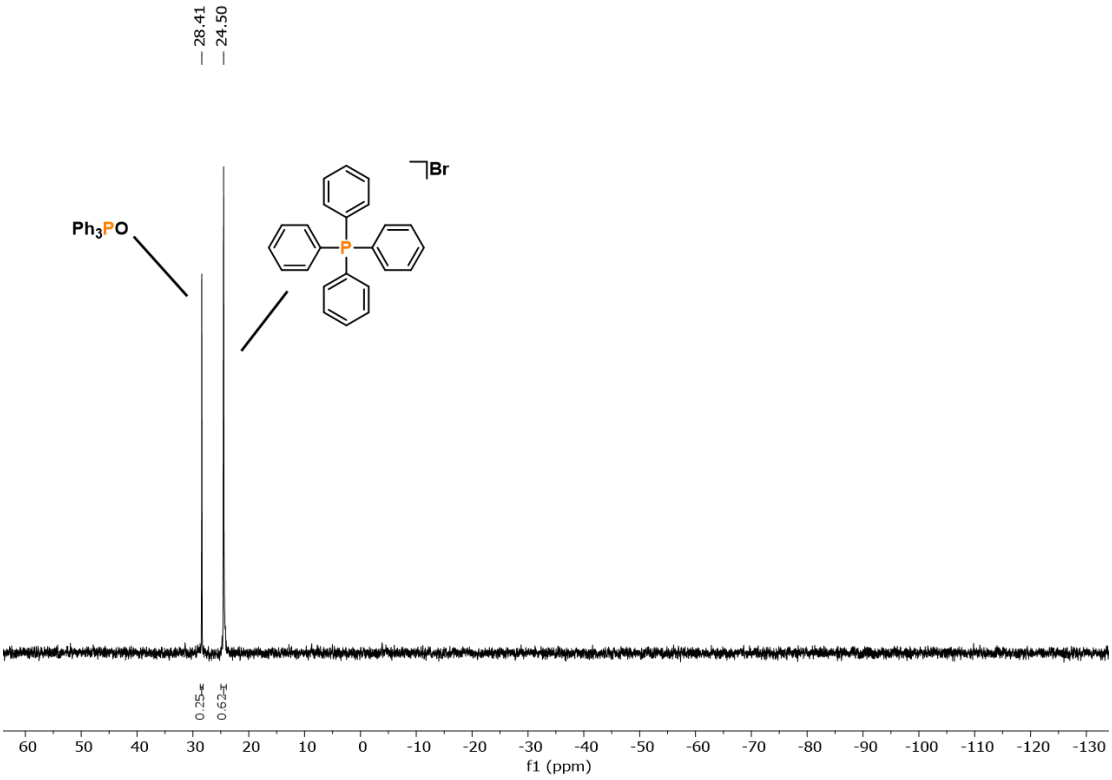


Figure S69. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photocatalytic functionalization of Ph_5P_5 using bromobenzene in a J. Young NMR tube after 20 h reaction time.

In addition, the mixture was subjected to $^{31}P\{^{1}H\}$ NMR analysis after 20 min, 1 h and 3 h. The progress of product formation was assessed with a standard capillary bearing Ph_3PO (0.03 mmol in MeCN-d_3). The NMR spectroscopic reaction monitoring is depicted in Figure S70. The phenylation of Ph_5P_5 with PhBr showed that the smaller cyclophosphine Ph_3P_3 is formed after irradiation for 20 min and can still be observed after irradiation for 1 h.[12] The cyclophosphane Ph_4P_4 is already present as a minor impurity in the starting material Ph_5P_5 but notably accumulates during initial irradiation for 20 min, after which it is almost completely consumed after 1 h reaction time. During this period, Ph_5P_5 is fully consumed, which is in alignment with the rapid consumption of P_4 in the NMR monitoring study (Figure S65 and Figure S68). After irradiation for 1 h (20 min), the P_1-intermediates $PhPH_2$ and Ph_2PH can be observed and are subsequently converted to Ph_3P and $[Ph_4P]Br$, which are the dominant reaction products after irradiation for 3 h. This indicates that the photocatalytic phenylation starting from a cyclopolyphosphine follows an analogous stepwise sequence as observed for P_4. Moreover, smaller cyclophosphines (or linear polyphosphorus species) should be accessible starting from P_4 and are eventually converted into P_1-species – however, their concentrations might be very low and their consumption fast, which prevents observation by ^{31}P NMR spectroscopy.

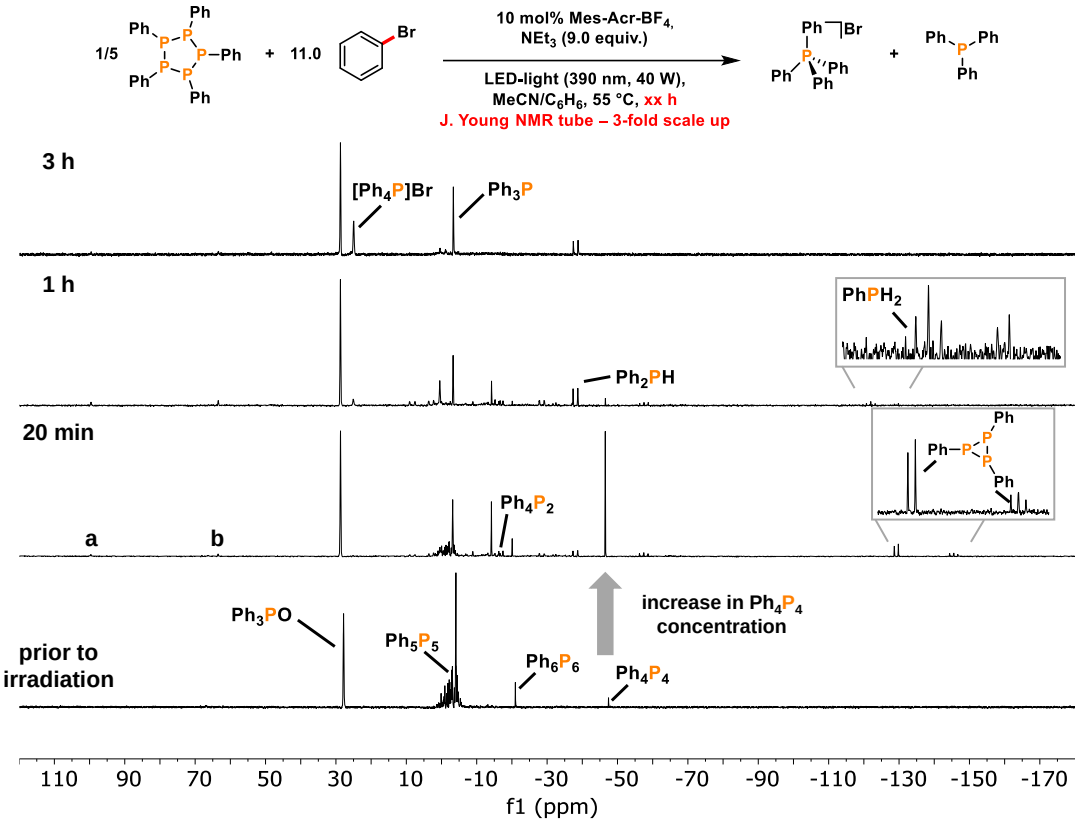
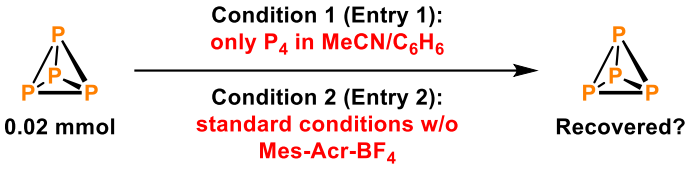


Figure S70. ^{31}P NMR reaction monitoring (161.98 MHz, MeCN-d_3, 300 K, NS 512 or NS 1024) of the phenylation of Ph_5P_5 in a J. Young NMR tube. Identification of cyclic polyphosphorus intermediates and side products in agreement with the literature.[1],[12] a: $PhP(NEt_2)_2$; b: $Ph_2P(NEt_2)$.

Stability of P_4 under irradiation:

A solution of P_4 (0.02 mmol) was irradiated either in a mixture of MeCN/C_6H_6 (3/2 v/v, overall 525.2 µL) or in a standard reaction mixture in the absence of photocatalyst (0.1 mL of MeCN was added instead; twofold scale up). Both initially clear, colourless solutions turn turbid after 20 h (only P_4: orange precipitation; with reagents: brown precipitation). ^{31}P{^{1}H} NMR spectroscopic analysis using the same pulse sequence (zgpg30, NS 256) as for the calibration shows only a resonance for residual P_4 (and internal standard Ph_3PO; Table S13 and Figure S71). 68% of the white phosphorus signal remained when only P_4 was irradiated and 74% of the P_4 signal intensity remained in the standard reaction mixture in the absence of photocatalyst. While P_4 partially decomposes when irradiated with nUV light, the formation of polyphosphorus species "P_nR_x" (with n = 2-4) or any other degradation product was not observed. Instead, it is likely that P_4 polmyerizes high(er)-molecular weight polyphosphorus species.

Table S13. Stability study of P_4 under irradiation with nUV light.



Entry	1	Full conv. of P_4?	✗	Remaining P_4 signal intensity	68%
	2		✗		74%

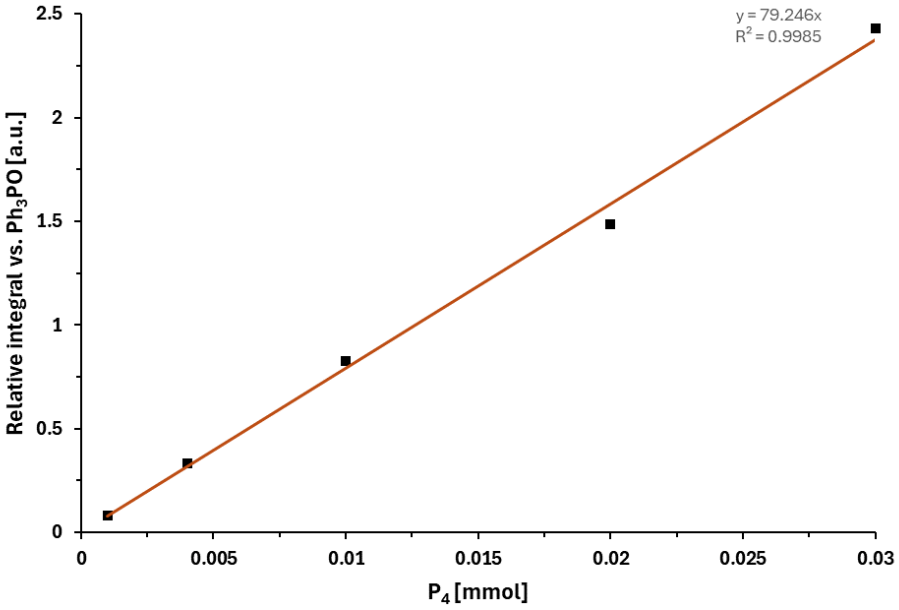
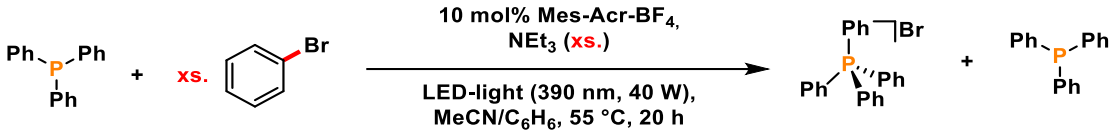


Figure S71. Plot showing the relative integral of a solution of P_4 vs. internal standard Ph_3PO (0.04 mmol) against the expected (based on mass added) molar quantities of P_4 (0.001 to 0.03 mmol) in a $MeCN/C_6H_6$ (3:2) solution using a $^{31}P\{^1H\}$ NMR experiment (zgpg30, NS 256).

S7. Photocatalytic phenylation of $PhPH_2$, Ph_2PH, Ph_4P_2 and Ph_3P and stability study with $[Ph_4P]Br$

To a 10 mL stoppered tube equipped with a stirring bar was added bromobenzene (0.0 to 0.44 mmol, 0.0 to 11.0 equiv. based on the phosphorus atom), NEt_3 (0.0 to 0.36 mmol, 0.0 to 9.0 equiv. based on the phosphorus atom), 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (Mes-Acr-BF_4; 2.3 mg, 4.0 µmol, 10 mol% based on the phosphorus atom) and the P-atom source ($Ph_{3-n}PH_n$ [n = 0-2], 0.04 mmol, 1.0 equiv. or Ph_4P_2, 0.02 mmol, 7.4 mg, 0.5 equiv. or $[Ph_4P]Br$, 16.8 mg, 0.04 mmol, 1.0 equiv.). The mixture was dissolved in acetonitrile/benzene (0.1 + 0.0655 mL). The tube was sealed, placed in a custom-made flask holder (Figure S2, left), and irradiated with nUV light (390 nm, 40 W, Kessil PR160L in a PR160 Rig with Fan Kit, Figure S2, right) for 20 h (unless stated otherwise). Ph_3PO (0.02 mmol, stock solution in benzene) was subsequently added to act as an internal standard. The resulting mixture was subjected to NMR analysis.

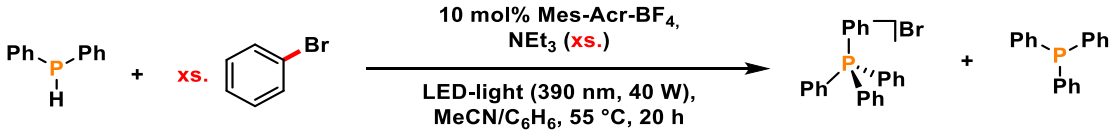
Table S14. Photochemical functionalization of Ph_3P to $[Ph_4P]Br$.[a]



Entry	Conditions[b] NEt_3:PhBr	Form. of $[Ph_4P]Br$ / %	Form. of Ph_3P / %	Intermediates	Consumption of Ph_3P / %
1	9:11	86	0	/	>99
2	3:5	97	0	/	>99
3	2:3	89	0	/	>99
4	9:0	0	0	Ph_2PH, $PhPH_2$[c]	70

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with Ph_3P (10.5 mg, 0.04 mmol). [b] Listed equivalents are defined per P atom. [c] A minor signal for $PhPH_2$ can be observed in the $^{31}P\{^1H\}$ NMR spectrum (NS 64).

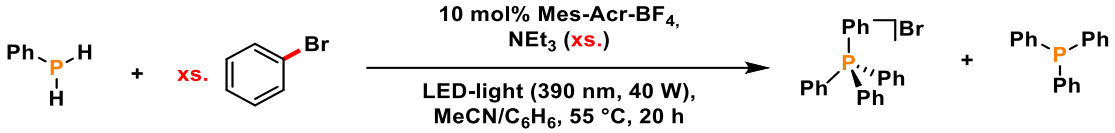
Table S15. Photochemical functionalization of Ph_2PH to $[Ph_4P]Br$.[a]



Entry	Conditions[b] NEt_3:PhBr	Form. of $[Ph_4P]Br$ / %	Form. of Ph_3P / %	Intermediates	Consumption of Ph_2PH / %
1	9:11	89	0[c]	/	>99
2	3:5	85	0[c]	/	>99
3	2:3	39	40	/	>99[d]
4	9:0	0	0	$PhPH_2$	68[e]

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with Ph_2PH (6.96 µL, 0.04 mmol). [b] Listed equivalents are defined per P atom. [c] A minor signal for Ph_3P can be observed in the $^{31}P\{^1H\}$ NMR spectrum (NS 64). [d] A minor signal for Ph_3P can be observed in the $^{31}P\{^1H\}$ NMR spectrum (NS 64). [e] Non-calibrated value assessed by integration of the signal in the single scan $^{31}P\{^1H\}$ NMR spectrum.

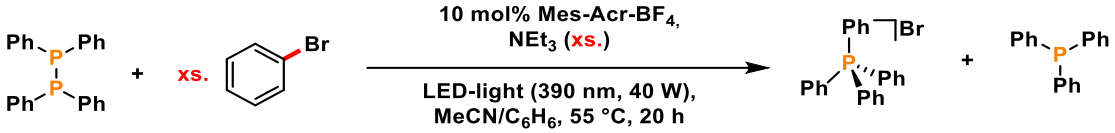
Table S16. Photochemical functionalization of $PhPH_2$ to $[Ph_4P]Br$.[a]



Entry	Conditions[b] NEt_3:PhBr	Form. of $[Ph_4P]Br$ / %	Form. of Ph_3P / %	Intermediates	Consumption of $PhPH_2$ / %
1	9:11	71	0	Ph_3P[c]	>99
2	6:8	64	6	/	>99
3	3:5	21	35	Ph_4P_2, Ph_2PH[d]	>99
4	9:0	0	0	/	37[e]

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with $PhPH_2$ (4.40 µL, 0.04 mmol). [b] Listed equivalents are defined per P atom. [c] A minor signal for Ph_3P can be observed in the $^{31}P\{^1H\}$ NMR spectrum (NS 64). [d] A minor signal for Ph_2PH can be observed in the $^{31}P\{^1H\}$ NMR spectrum (NS 64). [e] Non-calibrated value assessed by integration of the signal in the single scan $^{31}P\{^1H\}$ NMR spectrum.

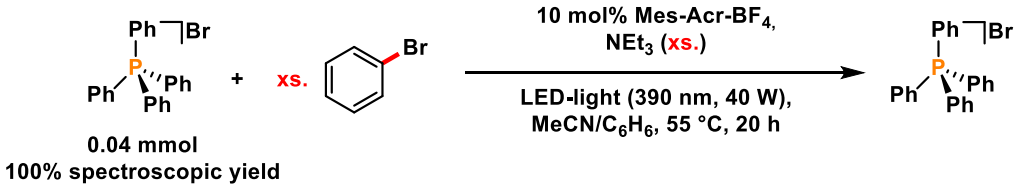
Table S17. Photochemical functionalization of Ph_4P_2 to $[Ph_4P]Br$.[a]



Entry	Conditions[b] NEt_3:PhBr	Form. of $[Ph_4P]Br$ / %	Form. of Ph_3P / %	Intermediates	Consumption of Ph_4P_2 / %
1	9:11	91	0	/	>99
2	3:5	82	0[c]	/	>99
3	2:3	72	19	/	>99
4	9:0	0	0	Ph_2PH, $PhPH_2$	>99

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with Ph_4P_2 (7.4 mg, 0.02 mmol). [b] Listed equivalents are defined per P atom. [c] A minor signal for Ph_3P can be observed in the $^{31}P\{^1H\}$ NMR spectrum (NS 64).

Table S18. Stability test of tetraphenylphosphonium bromide $[Ph_4P]Br$ toward photocatalytic conditions.[a]



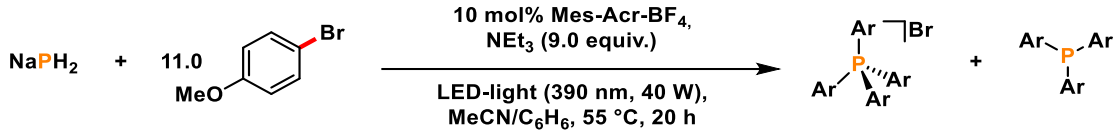
Entry	Conditions[b] NEt_3:PhBr	Recovered $[Ph_4P]Br$/ %	Formation of Ph_3P / %
1	9:11	81	/[c]
2	3:5	78	/[c]
3	9:0	41	52
4	0:0	97	/

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with $[Ph_4P]Br$ (16.8 mg, 0.04 mmol; 100% spectroscopic yield) for a stability check of the phosphonium salt under the photocatalytic reaction conditions. The phosphonium salt was fully dissolved in the reaction mixture. [b] Listed equivalents are defined per P atom. [c] No formation of Ph_3P or other phosphorus species was observed.

S8. Photocatalytic arylation of $NaPH_2$

To a 10 mL stoppered tube equipped with a stirring bar were added the appropriate aryl bromide (0.44 mmol, 11.0 equiv. based on the phosphorus atom), NEt_3 (50.2 µL, 0.36 mmol, 9.0 equiv. based on the phosphorus atom), 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (Mes-Acr-BF_4; 2.3 mg, 4.0 µmol, 10 mol% based on the phosphorus atom) and $NaPH_2$ (0.04 mmol, 2.2 mg, 1.0 equiv.). The mixture was dissolved in acetonitrile (0.1 mL). The tube was sealed, placed in a custom-made flask holder (Figure S2, left), and irradiated with nUV light (390 nm, 40 W, Kessil PR160L in a PR160 Rig with Fan Kit, Figure S2, right) for 20 h (unless stated otherwise). Ph_3PO (0.02 mmol, stock solution in benzene) was subsequently added to act as an internal standard. The resulting mixture was subjected to NMR analysis.

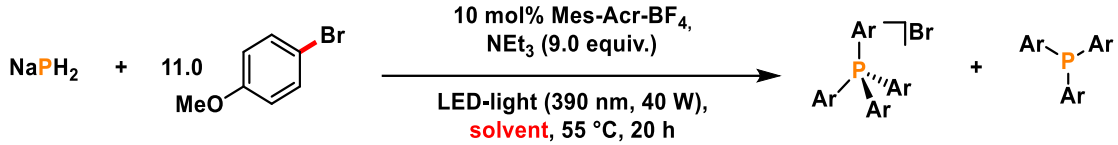
Table S19. Photocatalytic functionalization of $NaPH_2$ to $[Ar_4P]Br$ and Ar_3P: screening of control experiments.[a]



Entry	Conditions	Full conv. of $NaPH_2$?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	Standard	✓	32	4
2	No photocatalyst	✓	0	2
3	No light[b]	✓	0	0
4	No NEt_3	✓	0	4

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with $NaPH_2$ (2.2 mg, 0.04 mmol). Ar = 4-OMe–C_6H_4–. [b] The reaction flask was heated to 55 °C.

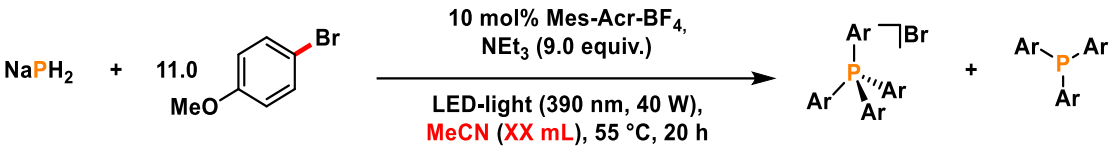
Table S20. Photocatalytic functionalization of $NaPH_2$ to $[Ar_4P]Br$ and Ar_3P: screening of solvents.[a]



Entry	Solvent	Full conv. of $NaPH_2$?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	Acetonitrile	✓	32	4
2	DMF	✓	5	6
3	DMSO	✓	13	0
4	Benzene	✓	8	0
5	Acetone	✓	14	0
6	THF	✓	6	2

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with $NaPH_2$ (2.2 mg, 0.04 mmol). Ar = 4-OMe–C_6H_4–. The general procedure (section S2) was modified to use the solvent system indicated (identical solvent volume).

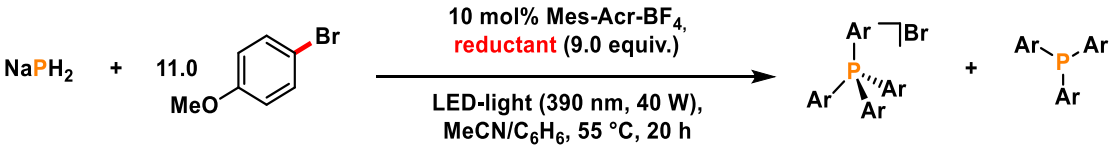
Table S21. Photocatalytic functionalization of $NaPH_2$ to $[Ar_4P]Br$ and Ar_3P: concentration screening.[a]



Entry	Solvent volume	Full conv. of $NaPH_2$?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	0.1 mL	✓	32	4
2	0.5 mL	✓	10	6
3	1.0 mL	✓	0	6
4	2.0 mL	✓	1	0

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with $NaPH_2$ (2.2 mg, 0.04 mmol). Ar = 4-OMe–C_6H_4–. The general procedure (section S2) was modified to use the indicated amount of MeCN.

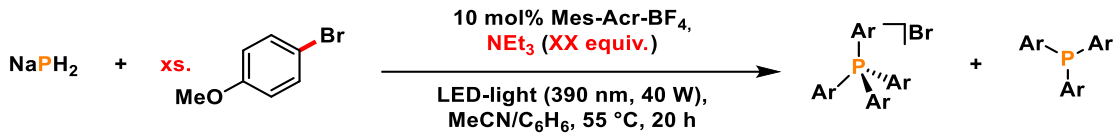
Table S22. Photocatalytic functionalization of $NaPH_2$ to $[Ar_4P]Br$ and Ar_3P: screening of reductants.[a]



Entry	Reductant	Full conv. of $NaPH_2$?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	NEt_3	✓	32	4
2	DIPEA	✓	24	5
3	N^nBu_3	✓	29	8
4	$NMe_2{}^nPr$	✓	9	5

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with $NaPH_2$ (2.2 mg, 0.04 mmol). Ar = 4-OMe–C_6H_4–. The general procedure (section S2) was modified to use the indicated reducing agent (identical stoichiometry).

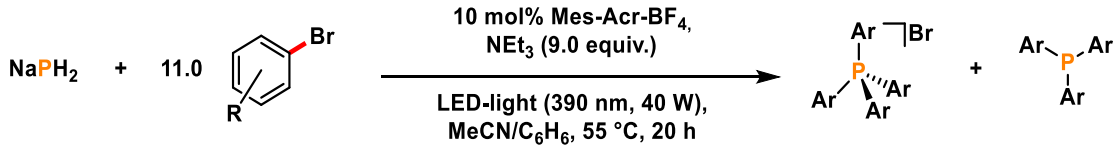
Table S23. Photocatalytic functionalization of $NaPH_2$ to $[Ar_4P]Br$ and Ar_3P: screening of reductant and substrate stoichiometry.[a]

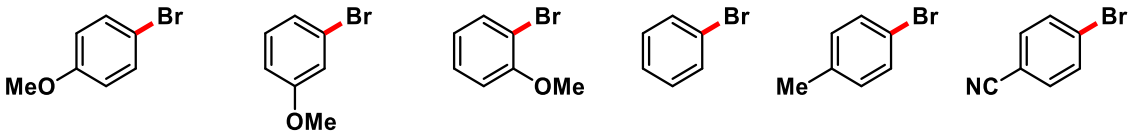


Entry	Stoichiometry NEt_3:4-Bromoanisole	Full conv. of $NaPH_2$?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	9:5	✓	11	6
2	9:7	✓	20	3
3	9:9	✓	30	5
4	9:11	✓	32	4
5	9:13	✓	21	3
6	9:15	✓	22	4
7	9:17	✓	27	3
8	3:11	✓	26	2
9	5:11	✓	30	2
10	7:11	✓	33	5
11	11:11	✓	20	5
12	13:11	✓	12	10
13	15:11	✓	7	6

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with $NaPH_2$ (2.2 mg, 0.04 mmol). Ar = 4-OMe–C_6H_4–.

Table S24. Photocatalytic functionalization of $NaPH_2$ to $[Ar_4P]Br$ and Ar_3P: screening of substrates.[a]





Entry	Substrate	Full conv. of $NaPH_2$?	Form. of $[Ar_4P]Br$ / %	Form. of Ar_3P / %
1	R = 4-OMe	✓	32	4
2	R = 3-OMe	✓	21	4
3	R = 2-OMe	✓	12	0
4	R = H	✓	19	0
5	R = 4-Me	✓	19	7
6	R = 4-CN	✓	7	0

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with $NaPH_2$ (2.2 mg, 0.04 mmol). The general procedure (section S2) was modified to use the indicated substrate (identical stoichiometry).

S8. References

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